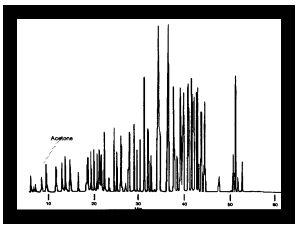
Guidance to the Performance and Presentation of Analytical Chemistry Data

$$s^2_{\text{Sampling}} + s^2_{\text{Preparation}} + s^2_{\text{Analysis}} = s^2_{\text{Total}}$$

+

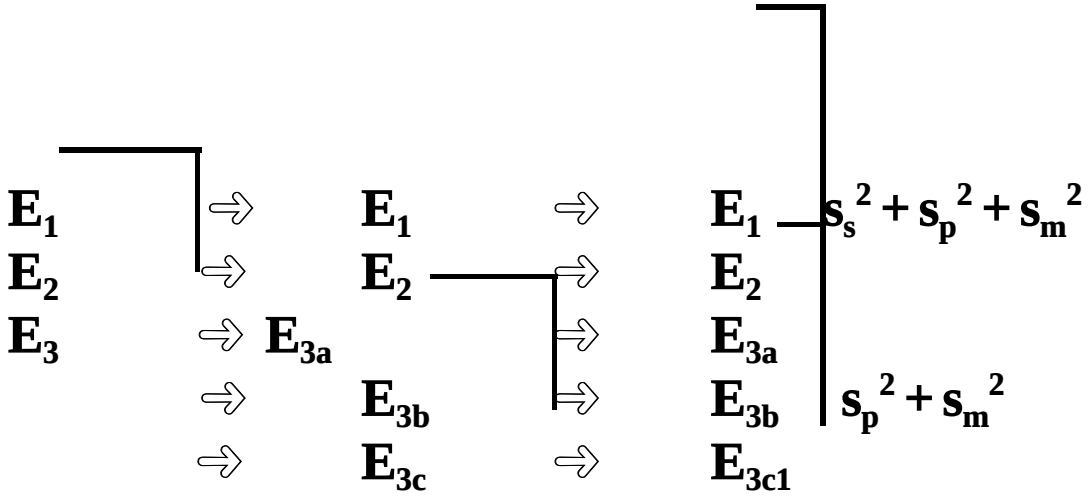
+



= Total Error

Error Error

Error



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Indiana Department of Environmental Management

Guidance to the Performance and Presentation of Analytical Chemistry Data

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Preface

The Indiana Department of Environmental Management (IDEM), is aware that there is ~~a~~ great need for a guidance document on generating valid analytical data that meets data quality objectives for environmental projects. This is not a simple task, especially given the wide range of methods, complex matrices, and variant project objectives possible in the environmental field. Sound guidance has become even more critical with the increasing use of risk assessment as an environmental tool, and with EPA's announcement of the intent to implement a Performance Based Measurement System for environmental monitoring. These concerns necessitate limiting the focus of this document to EPA methods with the most universal application.

The most versatile of promulgated EPA methods for analysis of environmental samples are the *Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods*, U.S. EPA Publication SW-846**,** Third Edition, November 1986, and promulgated Updates. (As of this writing, the current promulgated update is Final Update III, December, 1996.) The SW-846 methods include procedures for analyses of matrices ranging from water to sludges, including soils, sediments, and oils. Since the SW-846 methods have the most comprehensive range of application and most flexible quality assurance/quality control (QA/QC) requirements meeting most project objectives, these methods they have been chosen as the focus basis of this document The emphasis on SW-846 methods does not limit a facility or laboratory to using only SW-846 analytical methods. There will be cases where it will not be possible to use SW-846 methods for analysis, or where it will be more appropriate to choose alternate analytical methods. However, the data quality needs of the environmental project should be carefully evaluated before alternative methods are chosen. The QA principles found in this document can be applied to a wide variety of appropriate analytical methods.

A single document cannot cover all possible requirements to meet the Data Quality Objectives of every environmental project that may be encountered. There will be projects where the need for data certainty may be less than recommended in this guidance or projects where data certainty may need to be more stringent. However, this document will aid in making sound analytical judgements and can be used as a baseline for assessing the quality of data generated in relation to the Data Quality Objectives for a wide range of specific environmental projects.

For most environmental projects, some level of analytical data quality will be required to address the environmental concern under investigation. Furthermore, in most cases some level of quantitative certainty will have to be assessed. When data quality objectives require accurately quantitated analytical data with the level of uncertainty determined, certain fundamental questions must be addressed. These questions include:

Sampling Design Considerations

- Does the sampling methodology reflect the project objectives?
- Is sampling being conducted for the appropriate analytes?
- Is sampling being conducted in the appropriate environmental matrices?
- Have a sufficient number of samples been collected to meet project objectives?
- Were sample locations chosen appropriately?

Analytical and Data Validation Considerations

- Has the appropriate analytical method been selected (taking analyte, matrix, and project objectives into consideration?
- Is the instrument used for analysis operating correctly?
- Is the instrument signal to noise ratio adequate?
- Is the stated result within the calibration range of the instrument?
- Is the instrument stable?
- Is there any carryover between analyses?
- Has an artifact from outside the matrix entered the analysis system?
- Is there a matrix effect on the result?
- Can the analytical result be reproduced?
- Have all of the above been demonstrated and documented?

Data Assessment/Project Application Considerations

- Do the data exhibit a directional bias?
- What is the magnitude of any directional bias?
- What is the magnitude of the variability in the data?
- Do the data meet the project DQOs?
- Do the data answer the question the project was meant to address?

Determining whether these objectives have been attained requires a knowledge of the entire data acquisition process: from sampling design; through the analytical process (and the attendant control criteria**)**, documentation, and data validation; to data assessment and application to the project. An understanding of the project objectives and data quality objectives is also needed.

This document incorporates the concepts of the EPA Quality System into the sampling, analysis, data validation and data assessment process. These include the Quality Management Plan (QMP) and the Quality Assurance Project Plan (QAPP), which are introduced in Part I, and the Data Quality Objectives (DQO) Process, which is discussed in Part II. Part III provides a brief description of sampling design and field QA/QC requirements for the sampling process.

Part IV is adapted from SW-846 Chapter One, "Quality Control," (July 1992). It contains the guidance for performing quality assessments based on specific quality assurance/quality control principles and will

also aid in the preparation of quality assurance project plans. Part V contains specific guidance for analytical methods, techniques, and control criteria. Appendix A contains SW-846 Method 7000A (July 1992): the quality assurance/quality control requirement for analysis of metals by atomic absorption methods. Appendix B contains SW-846 Method 8000B (December 1996), the quality assurance/quality control requirements instrumental organic analysis by gas chromatography and high performance liquid chromatography. Appendix C contains a list of deliverables needed to document data results. Appendix D contains EPA's Performance Based Measurement System Draft Generic Checklists. The checklists can be use to validate method modifications or use of non-standard methods when required by project DQOs.

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TABLE OF CONTENTS

PART I.

Introduction to the Quality System
and
Project Documentation Hierarchy

PART I.

Introduction to the Quality System and Project Documentation Hierarchy

Overview of the EPA Quality System

The U.S. EPA (EPA) has established a Quality System (previously called a Quality Assurance Program) to support all environmental programs conducted by or on behalf of EPA. It is based on the American National Standard ANSI/ASQC E4-1994, *Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs*.[1]
EPA defines the Quality System as follows:

> EPA's Quality System is the means by which the Agency implements the quality management process. . . .
>
> **The Quality System applies to management systems and *the collection, evaluation, and use of environmental data*.** Also the Quality System is intended to apply to the design, construction, and operation of environmental technology.[2]

The IDEM is adopting the concepts of the EPA Quality System and feels that a Quality System is so important because environmental professionals, whether within the agency, in the regulated community, or in consulting firms:

> **make important decisions about complex issues that have *significant* environmental, social, health, and economic impacts and consequences.** To support these decisions, [environmental professionals] often collect data to gain a better scientific understanding of the environmental problem being studied. Although collecting data is necessary and in many cases required by law, it is also expensive. . . .By incorporating scientific and systematic planning processes, [the] Quality System helps organizations. . . conduct their data collection operations more efficiently and cost-effectively. The Quality System provides these organizations with management and project tools that can help them collect the right type, quantity, and quality of data needed to support scientifically sound and legally defensible decisions.[3]

The Quality System at the Program Level: the Quality Management Plan

The **Quality Management Plan (QMP)** is what organizations, or programs within organizations, use to document how they will plan, implement, and assess their quality system. It is a template defining the organization's quality assurance (QA) policies and procedures; the areas in which QA is applied; the

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[1]Environmental Protection Agency, Office of Research and Development, *The EPA Quality System: EPA QA/G-0 Final*, Pre-Publication Copy, August 1997, p.0-2.

[2]Ibid., p.0-1. (Emphasis added.)

[3]Ibid., p. 0-2. (Emphasis added.)

criteria for QA application; and the various QA-related roles, responsibilities, and authorities of program staff.[4] Elements of the QMP include:

- Management and Organization
- Quality System and Description
- Personnel Qualification and Training
- Procurement of Items and Services
- Documentation and Records
- Computer Hardware and Software
- Planning
- Implementation of Work Process
- Assessment and Response
- Quality Improvement[5]

The QMP is similar to what was formerly called a Quality Assurance Program Plan, or QAPP. The acronym QAPP is now used for the Quality Assurance Project Plan, formerly abbreviated as QAPjP.[6]

The Quality System at the Project Level: The Quality Assurance Project Plan

A **Quality Assurance Project Plan (QAPP)** is a formal technical document containing the detailed quality assurance, quality control (QC), and other technical procedures for assuring the quality of environmental data, prepared for *each* environmental data collection activity. **A QAPP is a site-specific, project-specific planning document and should be approved by the IDEM prior to collection of the data.**

For a given project (environmental data collection activity), the QAPP must demonstrate that:

- the project's technical and quality objectives are identified and agreed upon;
- the intended sampling procedures, field measurements, analytical methods, and other data acquisition methods are appropriate for achieving project objectives;
- the data assessment procedures are sufficient for confirming that data of the type and quality needed and expected are obtained; and
- any limitation on the use of the data can be identified and documented.[7]

A QAPP is composed of a number of elements that can be grouped into four categories:

- project management,
- measurement/data acquisition, and
- assessment/oversight,
- data validation and usability.

The number of elements that are included in a particular QAPP depends on the complexity of the project and the intended end use of the data. EPA has identified 25 elements that will generally be appropriate for inclusion in site-specific QAPPs. The QAPP for a particular project may not require the inclusion of

---

[4]Environmental Protection Agency, Office of Research and Development, *The EPA Quality System: EPA QA/G-0 Final*, Pre-Publication Copy, August 1997, p. 2-1.

[5]Ibid., p. 2-2.

[6]There are exceptions to the replacement of QAPjP with QAPP. E.g., at this writing, SW-846 Chapter One, "Quality Control" (July 1992), still uses the QAPjP acronym to abbreviate Quality Assurance Project Plan.

[7]Environmental Protection Agency, Office of Research and Development, *The EPA Quality System: EPA QA/G-0 Final*, Pre-Publication Copy, August 1997, p. 5-2.

all 25 elements. Other projects may require the to QAPP include additional information that is not contained in these elements. The 25 elements are listed below:

FIGURE 1[8]

QAPP Elements

A. Project Management

A1 Title and Approval Sheet
A2 Table of Contents
A3 Distribution List
A4 Project/Task Organization
A5 Problem Definition/Background
A6 Project/Task Description
A7 Quality Objectives and Criteria for Measurement Data
A8 Special Training Requirements/Certification
A9 Documentation and Records

B. Measurement/Data Acquisition

B1 Sampling Process Design (Experimental Design)
B2 Sampling Methods Requirements
B3 Sample Custody Requirements
B4 Analytical Methods Requirements
B5 Quality Control Requirements
B6 Instrument/Equipment Testing, Inspection, and Maintenance Requirements
B7 Instrument Calibration and Frequency
B8 Inspection/Acceptance Requirements for Supplies and Consumables
B9 Data Acquisition Requirements (Non-Direct Measurements)
B10 Data Management

C. Assessment/Oversight

C1 Assessments and Response Actions
C2 Reports to Management

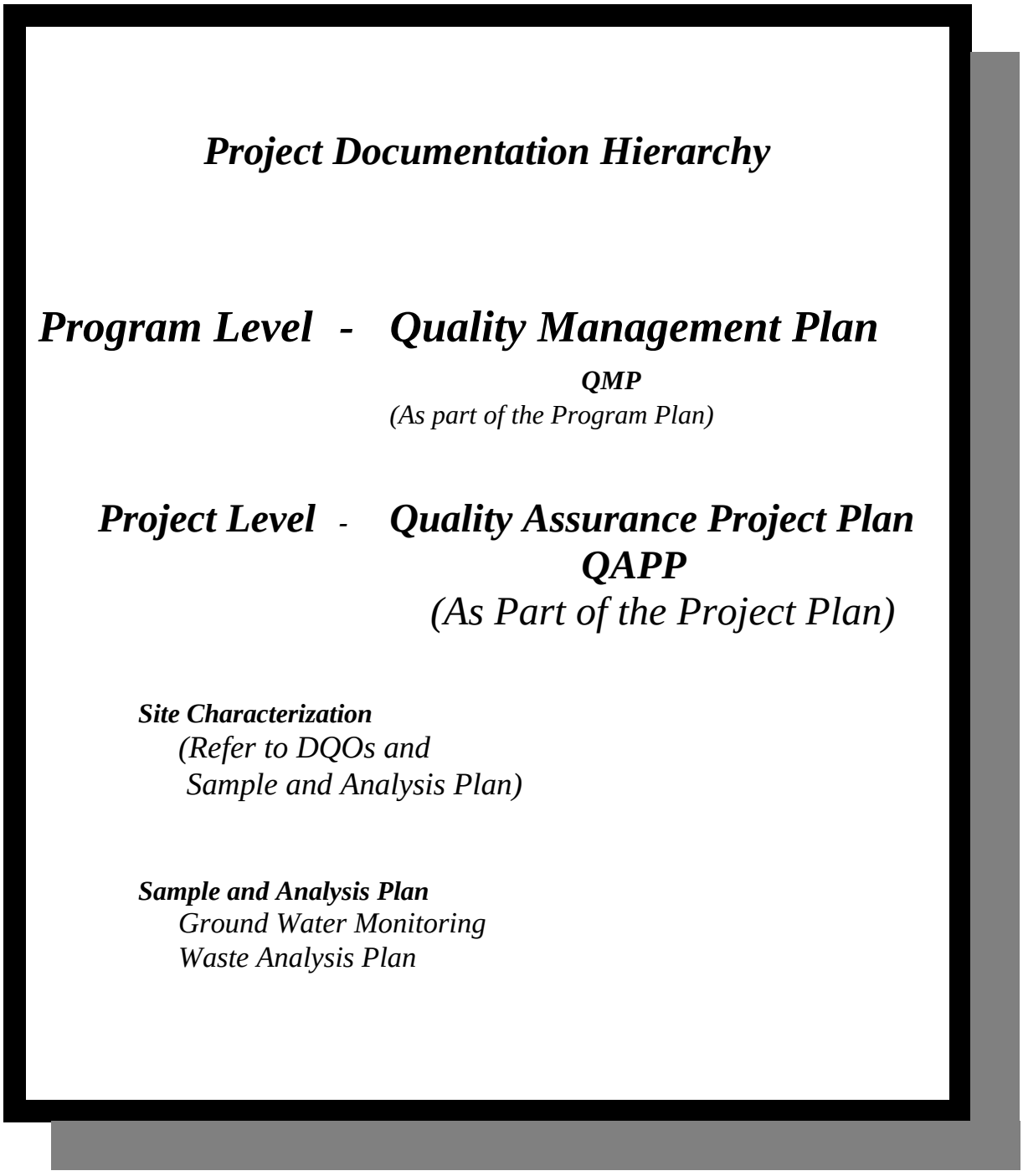
D. Data Validation and Usability

D1 Data Review, Validation, and
D2 Validation and Verification Methods

A diagram of project documentation hierarchy follows.

[8]Environmental Protection Agency, Office of Research and Development, *The EPA Quality System: EPA QA/G-0 Final*, Pre-Publication Copy, August 1997, p. 5-3.

FIGURE 2


Project Documentation Hierarchy
Program Level - Quality Management Plan
QMP
(As part of the Program Plan)
Project Level - Quality Assurance Project Plan
QAPP
(As Part of the Project Plan)
Site Characterization
(Refer to DQOs and
Sample and Analysis Plan)
Sample and Analysis Plan
Ground Water Monitoring
Waste Analysis Plan

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PART II.

The Data Quality Objectives Process

PART II.

Data Quality Objectives and the Data Quality Objectives Process

Integral to the development of the QAPP are the project **Data Quality Objectives (DQOs)**. A project may be viewed as a series of three phases: Planning, Implementation, and Assessment. The QAPP development may be viewed as the transition between the first two phases, Planning and Implementation. The first phase, Planning, consists of the development of the DQOs using the DQO process or a similar systematic planning process. The DQOs provide statements about the expectations and requirements of the data user (the environmental professional making a decision based on the data or final project report). In the QAPP these requirements are translated into QA/QC procedures and measurement performance specifications to be followed by personnel involved in the data acquisition, assessment, and presentation.[9]

EPA defines DQOs and the DQO development process as follows:

> **What are DQOs?** DQOs are qualitative and quantitative statements derived from the outputs of each step of the DQO Process that:
>
> 1) Clarify the study objective;
>
> 2) Define the most appropriate type of data to collect;
>
> 3) Determine the most appropriate conditions from which to collect the data; and
>
> 4) Specify acceptable levels of decision errors that will be used as the basis for establishing the quantity and quality of data needed to support the decision.
>
> The DQOs are then used to develop a scientific and resource-effective data collection design.
>
> **What is the DQO Process?** The DQO Process is a strategic planning approach based on the Scientific Method that is used to prepare for a data collection activity. It provides a systematic procedure for defining the criteria that a data collection design should satisfy, including when to collect samples, where to collect samples, the tolerable level of decision errors for the study, and how many samples to collect.
>
> By using the DQO Process, the [environmental professional] will assure that the type, quantity, and quality of environmental data used in decision making are appropriate for the intended application. In addition, the [environmental professional or responsible party] will guard against committing resources to data collection efforts that do not support a defensible decision.[10]

A **decision error** is an error made when drawing an inference from an environmental data set, such that variability or bias in the data misleads the decision maker into drawing a false conclusion about the actual

---

[9]Environmental Protection Agency, Office of Research and Development, *EPA Guidance for Quality Assurance Project Plans: EPA QA/G-5*, External Working Draft, November 1996, p. 1.

[10]Environmental Protection Agency, Office of Research and Development, *Guidance for the Data Quality Objectives Process: EPA QA/G-4*, EPA/600/R-96/055, September 1994, p. 1.

condition of the site being assessed[11]. The DQO Process allows decision makers to define their data requirements and acceptable levels of decision errors during planning, *before* any data are actually collected. Application of the DQO Process should result in data collection designs that will yield results of appropriate quality for defensible decision making.[12]

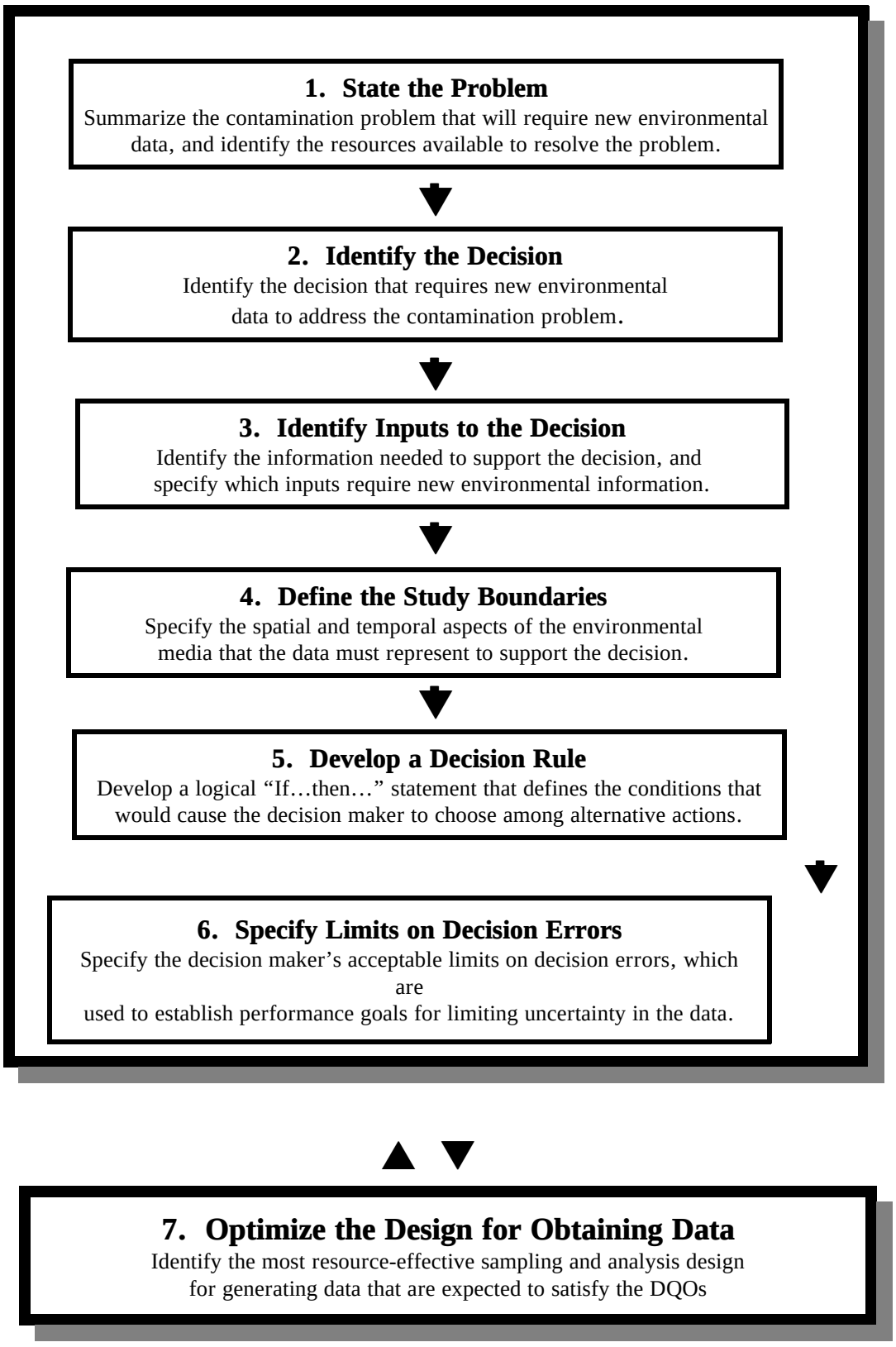
The steps of the DQO process are illustrated in Figure 3.

[11]Ibid., p. 66.

[12]Environmental Protection Agency, Office of Emergency and Remedial Response, *Data Quality Objectives Process for Superfund: Interim Final Guidance*, 9355.9-01, EPA540-R-93-071, September 1993, p. 1, NTIS, PB94-963203.

FIGURE 3[13]

The Data Quality Objective Process



[13]Environmental Protection Agency, Office of Emergency and Remedial Response, *Data Quality Objectives Process for Superfund: Interim Final Guidance*, 9355.9-01, EPA540-R-93-071, September 1993, p. 2, NTIS, PB94-963203.

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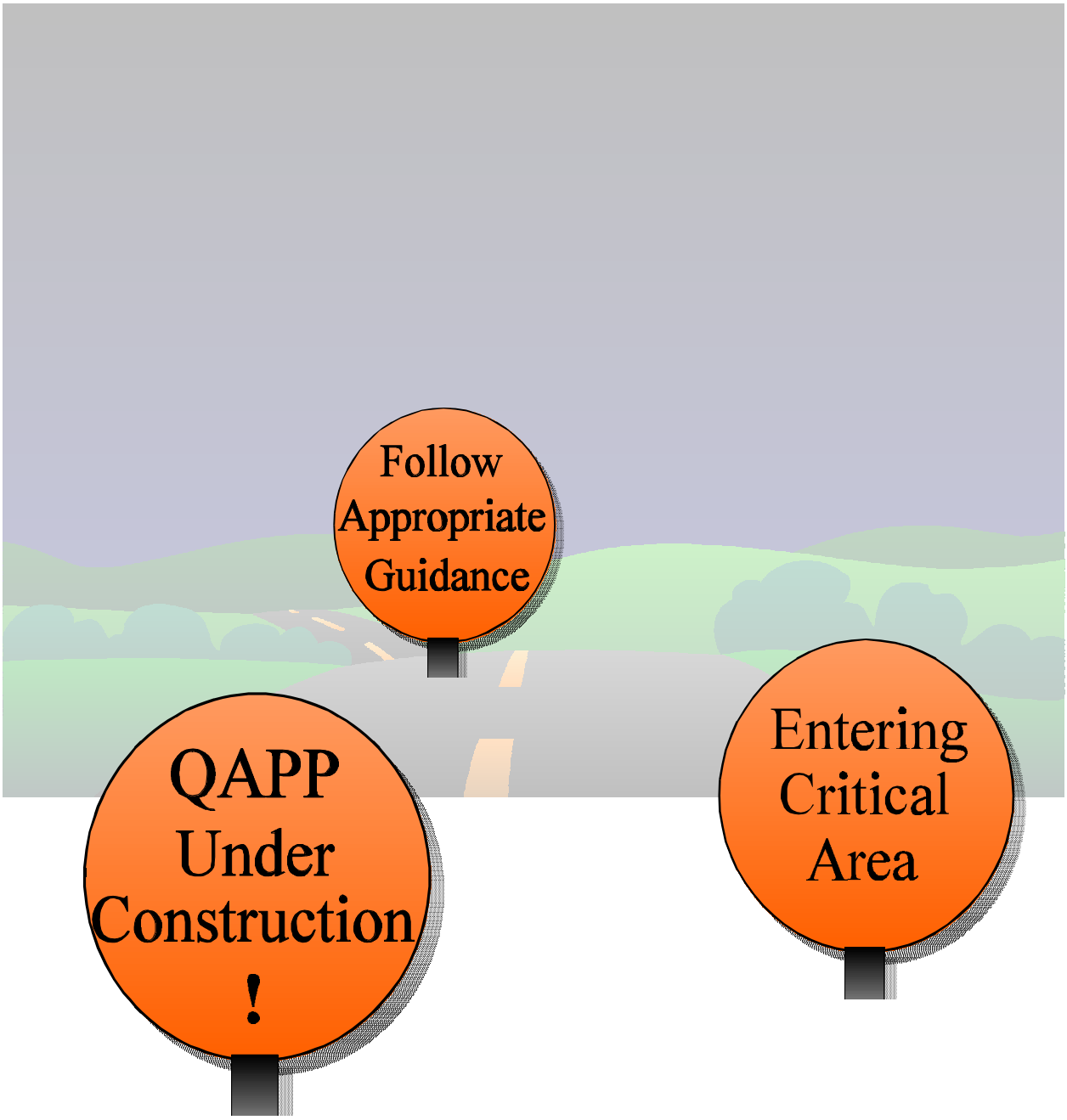
PART III.

Sampling Design
and
Field Quality Assurance/Quality Control

PART III.

Sampling Design and Field Quality Assurance/Quality Control



Objectives-Oriented Statistical Plan

When designing sampling for an environmental project, choose a statistical plan that meets the objectives of the QAPP. Reference applicable guidance or regulation, such as one or more of the following:

IDEM & EPA Guidance

- Title: *RISC: Risk-Integrated System of Cleanups*
  Type: IDEM Agency-Wide Guidance for Remediation Projects (all programs)
  Ref. No.: pending Draft Date: October 21, 1997

- Title: *Hazardous Waste Management Unit Closure Guidance*
  Type: IDEM Hazardous Waste Program Guidance (RCRA Treatment/Storage/Disposal units)
  Ref. No.: WASTE-0013-NPD Adopted: July 25, 1997

- Title: Solid Waste Program Plans
  Type: Solid Waste Program Rules (Indiana Administrative Code) for Land Disposal Units, E.g.:
  Ref. No.: 329 IAC 10-21 (Municipal Solid Waste Landfills: SAP, QAPP); 329 IAC 10-7 (Waste characterization requirements); 329 IAC 10-9-4 (Restricted waste sites waste criteria)
  Adopted: December 12, 1995 Effective: April 13, 1996

- Title: *Soil Screening Guidance: User's Guide*
  Type: U.S. EPA Office of Solid Waste and Emergency Response Guidance
  Ref. No.: EPA/540/4-96-/018 (NTIS: PB96-963505) Adopted: April 1996

- Title: *Soil Screening Guidance: Technical Background Document*
  Type: U.S. EPA Office of Solid Waste and Emergency Response Guidance
  Ref. No.: EPA/540/4-95-/128 (NTIS: PB96-963502) Adopted: May 1996

- Title: *Risk Assessment Guidance for Superfund Risk Assessment Guidance for Superfund, Volume I, Human Health Evaluation Manual: (Part A)*
  Type: U.S. EPA Office of Emergency and Remedial Response Guidance
  Ref. No.: EPA/540/1-89/002 Adopted: December 1989

- Title: *Risk Assessment Guidance for Superfund Risk Assessment Guidance for Superfund, Volume I, Human Health Evaluation Manual: (Part B, Development of Risk-based Preliminary Remediation Goals)*
  Type: U.S. EPA Office of Emergency and Remedial Response Guidance
  Ref. No.: Publication 9285.7-01B Adopted: December 1991

- Title: *A Compendium of Superfund Field Operations Methods*
  Type: U.S. EPA Office of Emergency and Remedial Response Guidance
  Ref. No.: EPA/540/P-87/001 Adopted: December 1987

- Title: *RCRA Ground-Water Monitoring Draft Technical Guidance*
  Type: U.S. EPA Office of Solid Waste Guidance
  Ref. No.: EPA/530/R-93/001 Draft Date: November 1992

- Title: *Proposed Guidelines for Ecological Risk Assessment*
  Type: U.S. EPA Guidance (Interoffice)
  Ref. No.: EPA/630/R-95/002B Adopted: August 1996

- *Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods*: SW-846, Third Edition. Volume Two, Part III, "Sampling" (Chapters Nine - Thirteen). 1986. U.S. EPA Office of Solid Waste and Emergency Response.

Statistical Sampling Publications

- Gibbons, Robert D. 1994. *Statistical Methods for Groundwater Monitoring*. New York: John Wiley & Sons, Inc.

- Gilbert, Richard O. 1987. *Statistical Methods for Environmental Pollution Monitoring*. New York: Van Nostrand Reinhold Company.

- Ott, Lyman. 1988. *An Introduction to Statistical Methods and Data Analysis*, 3rd ed.. Boston: PWS-Kent Publishing Company

Sampling Plan

Develop a sampling plan based on chemicals of concern (COCs) and sample matrices that meets the objectives o f the QAPP, ensuring that appropriate QA/QC measures are followed. Refer to:

- Part IV (**Quality Assurance/Quality Control Principles and QAPP Preparation**), Section 3.0 "Field Operations" of this document;

- Appendix II of this document, "Reporting and Deliverables: Quality Assurance/Quality Control Documentation Required";

- "CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES FOR AQUEOUS SAMPLES"
  (See following pages of this document.)

- Field Site Information Sheet Examples and Field Sample Sheet Examples (See following pages.)

- Chain-of-Custody Sheet Example (See following pages.)

CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES FOR AQUEOUS SAMPLES[14]

Analysis Name	Container*	Preservation	Max. Holding Time
Bacteriological Tests:			
Coliform, fecal and total	P,G	Cool, 4 C, 0.008%, $Na_2S_2O_3$	6 hours
Fecal streptococci	P,G	Cool, 4 C, 0.008%, $Na_2S_2O_3$	6 hours
Metals:			
Chromium VI	P,G	Cool, 4 C	24 hours
Mercury	P,G	HNO_3 to pH < 2	28 days
Metals (except chromium VI and mercury)	P,G	HNO_3 to pH < 2	6 months
Inorganic Tests:			
Acidity	P,G	Cool, 4 C	14 days
Alkalinity	P,G	Cool, 4 C	14 days
Ammonia	P,G	Cool, 4 C, H_2SO_4 to pH < 2	28 days
Biochemical oxygen demand	P,G	Cool, 4 C	48 hours
Bromide	P,G	None required	28 days
Biochemical oxygen demand Carbonaceous	P,G	Cool, 4 C	48 hours
Chemical oxygen demand	P,G	Cool, 4 C, H_2SO_4 to pH < 2	28 days
Chloride	P,G	None required	28 days
Chloride, total residual	P,G	None required	Analyze immediately
Color	P,G	Cool, 4 C	48 hours
Cyanide, total and amenable to chlorination	P,G	Cool, 4 C, NaOH to pH > 12 0.6g ascorbic acid	14 days
Fluoride	P	None required	28 days
Hardness	P,G	HNO_3 to pH < 2, H_2SO_4 to pH < 2	6 months
Hydrogen ion (pH)	P,G	None required	Analyze immediately
Kjeldahl and organic	P,G	Cool, 4 C, H_2SO_4 to pH < 2	28 days
Nitrate	P,G	Cool, 4 C	48 hours
Nitrate-nitrite	P,G	Cool, 4 C, H_2SO_4 to pH < 2	28 days
Nitrite	P,G	Cool, 4 C	48 hours
Oil and grease	G	Cool, 4 C, H_2SO_4 to pH < 2	28 days
Organic carbon	P,G	Cool, 4 C, HCl or H_2SO_4 to pH < 2	28 days
Orthophosphate	P,G	Filter immediately, cool, 4 C	48 hours
Oxygen, Dissolved Probe	G (bottle & top)	None required	Analyze immediately
Winkler	do	Fix on site and store in dark	8 hours
Phenols	G only	Cool, 4 C, H_2SO_4 to pH < 2	28 days
Phosphorus (elemental)	G	Cool, 4 C	48 hours
Phosphorus, total	P,G	Cool, 4 C, H_2SO_4 to pH < 2	28 days
Residue, total	P,G	Cool, 4 C	7 days
Residue, Filterable	P,G	Cool, 4 C	7 days
Residue, Nonfilterable (TSS)	P,G	Cool, 4 C	7 days
Residue, Settleable	P,G	Cool, 4 C	48 hours
Residue, Volatile	P,G	Cool, 4 C	7 days

***Polyethylene (P) or Glass (G)

[14]Adapted from *SW-846*, Third Edition, (September 1996), Chapter Two, Table 2-16, Rev. 0, TWO-31,32.

CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES FOR AQUEOUS SAMPLES

Analysis Name	Container*	Preservation	Max. Holding Time
Silica	P	Cool, 4 C	28 days
Specific conductance	P,G	Cool, 4 C	28 days
Sulfate	P,G	Cool, 4 C	28 days
Sulfide	P,G	Cool, 4 C, add zinc acetate Plus sodium hydroxide pH > 9	7 days
Sulfite	P,G	None required	Analyze immediately
Surfactants	P,G	Cool, 4 C	48 hours
Temperature	P,G	None required	Analyze
Total organic carbon (TOC)	P,G	Cool, 4 C, HCl or H_2SO_4 to pH < 2	28 days
Turbidity	P,G	Cool, 4 C	48 hours
Organic Tests:			
Purgeable halocarbons	G, Teflon-lined septum	Cool, 4 C, 0.008%, $Na_2S_2O_3$	14 days
Purgeable aromatic hydrocarbons	G, Teflon-lined septum	Cool, 4 C, 0.008%, $Na_2S_2O_3$, HCl to pH2	14 days
Acrolein and acrylonitrile	G, Teflon-lined septum	Cool, 4 C, 0.008%, $Na_2S_2O_3$, Adjust pH to 4-5	14 days
Phenols	G, Teflon-lined cap	Cool, 4 C, 0.008%, $Na_2S_2O_3$	7 days until extraction 40 days after extraction
Benzidines	G, Teflon-lined cap	Cool, 4 C, 0.008%, $Na_2S_2O_3$	7 days until extraction
Phthalate esters	G, Teflon-lined cap	Cool, 4 C	7 days until extraction 40 days after extraction
Nitrosamines	G, Teflon-lined cap	Cool, 4 C, store in dark, 0.008%, $Na_2S_2O_3$	40 days after extraction
PCBs, acrylonitrile	G, Teflon-lined cap	Cool, 4 C	40 days after extraction
Nitroaromatics and isophorone	G, Teflon-lined cap	Cool, 4 C, 0.008%, $Na_2S_2O_3$ store in dark	40 days after extraction
Polynuclear aromatic hydrocarbons	G, Teflon-lined cap	Cool, 4 C, 0.008%, $Na_2S_2O_3$ store in dark	40 days after extraction
Haloethers	G, Teflon-lined cap	Cool, 4 C, 0.008%, $Na_2S_2O_3$ store in dark	40 days after extraction
Chlorinated hydrocarbons	G, Teflon-lined cap	Cool, 4 C	40 days after extraction
TCDD	G, Teflon-lined cap	Cool, 4 C, 0.008%, $Na_2S_2O_3$	40 days after extraction
Total organic halogens (TOX)	G, Teflon-lined cap	Cool, 4 C, H_2SO_4 to pH < 2	7 days
Pesticides Tests:			
Pesticides	G, Teflon-lined cap	Cool, 4 C, pH 5-9	40 days after extraction
Radiological Tests:			
Alpha, beta and radium	P,G	HNO_3 to pH < 2	6 months

*****Polyethylene (P) or Glass (G)

SAMPLE CUSTODY CHAIN

I certify the following samples were collected by me or in my presence.

Signature

LAB ID NUMBER ASSIGNED	IDEM CONTROL NUMBER	SAMPLE IDENTIFICATION OR MONITORING WELL NUMBER	NUMBER OF CONTAINERS		COLLECTION			
			GLASS	PLASTIC	DATE	TIME	AM	PM

MAXIMUM AND MINIMUM TEMPERATURES DURING COLLECTION AND TRANSPORT: MAX MIN

TEMPERATURE OF SAMPLE AT EXCHANGE OF CUSTODY:

TRANSFER OF CUSTODY

I certify that I received the above samples.

Relinquished by: *(Signature)*			Received by: *(Signature)*		
TITLE	DATE	TIME	TITLE	DATE	TIME
		AM / PM			AM / PM
Relinquished by: *(Signature)*			Received by: *(Signature)*		
TITLE	DATE	TIME	TITLE	DATE	TIME
		AM / PM			AM / PM
Relinquished by: *(Signature)*			Received by: *(Signature)*		
TITLE	DATE	TIME	TITLE	DATE	TIME
		AM / PM			AM / PM

LABORATORY RECEIPT OF SAMPLES

I certify that I received the above Samples. After recording these samples into the official logbook, they will remain in the custody of competent lab personnel or be secured in a locked area at all times.

Signature	Laboratory
Date	Time AM/PM

Copies to be maintained by sampler and Laboratory. Original to be returned to IDEM with data package.

INDIANA DEPARTMENT OF ENVIRONMENTAL MANAGEMENT
OFFICE OF_____

GROUND WATER MONITORING - SITE INFORMATION SHEET

Site: _____ County: _____ Control Numbers: _____ - _____

Site Location (city first): _____ Sampling Date(s): _____

Site Sampler(s): _____ Company: _____

IDEM Samplers: _____ Laboratory: _____

Weather Conditions: Sky _____ Ground _____ Wind _____ Temp _____ Humidity _____

Purge and Sampling Equipment

Pump: Type _____ Size _____
Make _____ Tubing Material _____

Bailer: Material _____ Rope Material _____
Length _____ inches Diameter _____ inches Capacity _____ Liters / gallons

Purge and Sampling notes: _____

Field Analysis Equipment

Parameter	Meter / Equipment Model
Temperature	_____
pH	_____
Spec. Cond.	_____
Eh	_____
Diss. Oxygen	_____

Field Filtering Information

Filtered by: Facility / Consultant / IDEM
Filtration method: gravity / vacuum / pressure
Device type: _____
Filter: cartridge / paper make _____
size _____
pore _____

Meter Calibration notes: _____

Sample container source: _____ Sample preservative source: _____

Blank water source: _____ Decontamination water source: _____

Final Report

Photos taken? YES / NO Send analytical report to: _____ Phone: _____
Other Notes or Deviations from Sampling Plan: _____

 Sampler Signature: _____ Date: _____

Site: _____

County: _____

INDIANA DEPARTMENT OF ENVIRONMENTAL MANAGEMENT

OFFICE OF_____

GROUND WATER MONITORING - SAMPLE SHEET

Well / Sample I.D.: _____ IDEM Control #:_____

Field Tests		Sample Type	Preservative	Amount
Temperature:	_____ °C	Monitoring Well	HNO_3	_____
pH:	_____ std. units	Residential Well	H_2SO_4	_____
Spec. Cond.:	_____ umhos/cm	Duplicate of: _____	NaOH	_____
TDS:	_____ mg/L	Split		Zn-Acetate _____
Eh:	_____ mV	Blank: field / trip / equipment	HCl	_____
Diss. Oxygen:	_____ mg/L	_____		_____
				_____

Sample Date: ____ / ____ / ____ Sample Time: ____ : ____ AM / PM

Containers	Quantity
1 Liter Plastic	_____
1 Liter Glass	_____
40 mL Vials	_____
250 mL Glass	_____
500 mL Glass	_____
125 mL Plastic	_____
_____	_____

Monitoring Well Data

Well I.D.: _____

Reference Point on: inner casing / outer casing / none

Casing Stick-up: _____ ft

Total Well Depth: _____ ft

Depth to Water: _____ ft

Well Material: PVC / Stainless Steel / Teflon

Inside Diameter: 1 / 2 / 4 / 6 inch(es)

Well Purge Observations

Purge observed by IDEM? YES / NO Purge Date: ____ / ____ / ____

Purge Start: ____ : ____ AM / PM Purge Stop: ____ : ____ AM / PM Volume Purged: _____ gallons

Purged Approximately: 1 / 2 / 3 / 4 / 5 / > 5 well volumes Purged to dryness? YES / NO

Other Purge notes:

_____

_____

Well Sampling Observations

Sample Appearance: clear / slightly turbid / very turbid Color: gray / brown / _____

Were Metals samples filtered prior to preservation? YES / NO

Appearance of water subsequent to filtration: _____

Reaction upon addition of preservatives? YES / NO Explanation: _____

Other Sampling notes: _____

_____

Deviations from Sampling Plan: _____

_____

Rev. Date 4/30/98 Sampler Signature: _____ Date: _____

INDIANA DEPARTMENT OF ENVIRONMENTAL MANAGEMENT
OFFICE OF_____

SITE INFORMATION SHEET

Site: _____ County: _____ Control Numbers: _____ - _____

Site Location (city first): _____ Sampling Date(s): _____

Site Representative: _____ IDEM Sampler(s):_____

Weather Conditions: Sky _____ Ground _____ Wind _____ Temp _____

Containers	Total #	Preservatives	Lot #
1 Liter Plastic	_____	HNO_3	_____
1 Liter Glass	_____	H_2SO_4	_____
40 mL Vials	_____	NaOH	_____
500 mL Glass	_____	Zn-Acetate	_____
125 mL Plastic	_____	HCl	_____
_____	_____	Samples Iced?	YES / NO
Container Source: _____		Preservative Source: _____	

Sample Types: (circle all applicable)

	Ditch	Creek	River	Leachate
Waste Pile	Sediment	Drainage Tile	Soil	Residential Well
	Other_____	Lagoon	Pond	

Sampling Plan and Procedures

Briefly explain sampling objectives:

_____

_____

Expected constituents:

_____

Sampling equipment used:

_____

_____

Decontamination procedures used: _____

_____

Decontamination water source: _____ Blank water source: _____

Final Report

Photos taken? YES / NO Send analytical report to: _____ Phone: _____

Sampler Signature: _____ Date: _____

Page _____ of _____
Site: _____
County: _____

INDIANA DEPARTMENT OF ENVIRONMENTAL MANAGEMENT
OFFICE OF _____

SAMPLE SHEET

Sample Identification: _____ IDEM Control #: _____

Sample Date: _____ / _____ / _____ Sample Time: _____ : _____ AM / PM

Containers	Quantity	Preservatives	Amount
1 Liter Glass	_____	HNO_3	_____
1 Liter Glass	_____	H_2SO_4	_____
40 mL Vials	_____	NaOH	_____
500 mL Glass	_____	Zn-Acetate	_____
125 mL Plastic	_____	HCl	_____
_____	_____	No preservatives used for non-aqueous samples	

Field Measurements
Temperature _____ °C pH _____ Spec. Cond. _____ umhos/cm

Sample Type: (circle all applicable): Creek River Leachate Waste Pile
Ditch Drainage Tile Soil Residential Well
Sediment Lagoon Pond Other _____
Duplicate of _____ Equipment Blank Trip Blank

Sample Description
Sample location information: (location marker, depth taken, flow rate, vegetation damage, wildlife present, etc.)

_____

_____

Sample appearance and observations: (color, odor, clarity, suspended solids, reaction to preservatives, etc.)

_____

_____

Deviations from Sampling Plan:
_____

Other Notes: _____

Sampler Signature: _____ Date: _____

RISC and PRG Compounds on Method 8260 (GC/MS) List

Nonhalogenated Compounds (Includes nonaromatic alcohols, aldehydes, amines, esters, ethers, ketones, nitriles, and related compounds)	**Aromatic and Halogenated Compounds** (Includes **BTEX**, benzene derivatives, and chlorinated and brominated compounds **)**
Method 8015B - GC/FID	**Method 8021 - GC/PID-ELCD**
Acetone Acetonitrile Acrolein Acrylonitrile Allyl alcohol n-Butanol t-Butyl alcohol Crotonaldehyde Diethyl ether 1,4-Dioxane Ethanol Ethyl acetate Ethylene oxide Isobutyl alcohol Isopropyl alcohol Methanol Methyl ethyl ketone Methyl isobutyl ketone Paraldehyde 2-Pentanone 2-Picoline 1-Propanol Propionitrile Pyridine o-Toluidine	**Benzene** **Toluene** **Ethylbenzene** **Xylenes** **BTEX** Allyl chloride Benzyl chloride Bromoacetone Bromobenzene Bromochloromethane Bromodichloromethane Bromoform Bromomethane n-Butylbenzene sec-Butylbenzene tert-Butylbenzene Carbon tetrachloride Chlorobenzene Chlorodibromomethane Chloroethane 2-Chloroethanol 2-Chloroethyl vinyl ether Chloroform Chloroprene Chloromethane 2-Chlorotoluene 4-Chlorotoluene 1,2-Dibromo-3-chloropropane 1,2-Dibromoethane Dibromomethane 1,2-Dichlorobenzene 1,3-Dichlorobenzene 1,4-Dichlorobenzene Dichlorodifluoromethane 1,1-Dichloroethane 1,2-Dichloroethane 1,1-Dichloroethene cis-1,2-Dichloroethane trans-1,2-Dichloroethane 1,2-Dichloropropane 1,3-Dichloropropane 2,2-Dichloropropane 1,3-Dichloro-2-propanol 1,1-Dichloropropene cis-1,3-Dichloropropene trans-1,3-Dichloropropene Epichlorohydrin Hexachlorobutadiene Isopropylbenzene p-Isopropyltoluene Methylene chloride Naphthalene n-Propylbenzene Styrene 1,1,1,2-Tetrachloroethane 1,1,2,2-Tetrachloroethane Tetrachloroethene 1,2,3-Trichlorobenzene 1,2,4-Trichlorobenzene 1,1,1-Trichloroethane 1,1,2-Trichloroethane Trichloroethene Trichlorofluoromethane 1,2,3-Trichloropropane 1,2,4-Trimethylbenzene 1,3,5-Trimethylbenzene Vinyl chloride
***RISC* Volatile Organic Compounds Listed Only for Method 8260:**	
Methyl t-butyl ether (MTBE)	

RISC and PRG Compounds on Method 8270 (GC/MS) List				
Phenols	**Phthalate Esters**	**Organochlorine Pesticides**	**Polychlorinated Biphenyls (PCBs)**	**Nitroaromatics and Cyclic Ketones**
Method 8041-GC/FID-ECD	**Method 8061 - GC/ECD**	**Method 8081-GC/ECD-ELCD**	**Method 8082 -GC/ECD-ELCD**	**Method 8091 - GC/ECD**
2-Chlorophenol 2,4-Dichlorophenol 2,4-Dimethylphenol 2,4-Dinitrophenol 2-Methylphenol 3-Methylphenol 4-Methylphenol 4-Nitrophenol Phenol 2,4,5-Trichlorophenol 2,4,6-Trichlorophenol *and related compounds*	Bis(2-ethylhexyl)phthalate Butyl benzyl phthalate Di-n-butyl phthalate Diethyl phthalate Dimethyl phthalate Di-n-octyl phthalate *and related compounds*	Aldrin Captafol Chlorobenzilate Chlordane 4,4'-DDD 4,4'-DDE 4,4'-DDT Diallate Dieldrin Endosulfan Endosulfan sulfate Endrin α-HCH (α-BHC) -HCH (-BHC) -HCH (Lindane) Heptachlor Heptachlor epoxide Hexachlorobenzene Hexachlorocyclopentadiene Methoxychlor Mirex Toxaphene Trifluralin *and related compounds*	*PCBs as Aroclors:* Aroclor 1016 Aroclor 1221 Aroclor 1232 Aroclor 1242 Aroclor 1248 Aroclor 1254 Aroclor 1260 *Individual PCB Congeners:* 2-Chlorobiphenyl 2,3-Dichlorobiphenyl 2,2',5-Trichlorobiphenyl 2,4',5-Trichlorobiphenyl 2,2',3,5'-Tetrachlorobiphenyl 2,3',4,4'-Tetrachlorobiphenyl 2,2',3,4,5'-Pentachlorobiphenyl 2,2',4,5,5'-Pentachlorobiphenyl etc. 2.2',3,3',4,4',5,5',6-Nonachloro-biphenyl	1,2-Dinitrobenzene 1,3-Dinitrobenzene 1,4-Dinitrobenzene 2,4-Dinitrotoluene 2,6-Dinitrotoluene Nitrobenzene Pentachloronitrobenzene Trifluralin

RISC and PRG Compounds on Method 8270 (GC/MS) List, continued

Haloethers	Chlorinated Hydrocarbons	Aniline and Selected* Derivatives	Organophosphorus Compounds	Polynuclear Aromatic Hydrocarbons
Method 8111 - GC/ECD	**Method 8121 - GC/ECD**	**Method 8131-GC/NPD**	**Method 8141-GC/NPD**	**Method 8310 - HPLC/UV-Fluorescence**
Bis(2-chloroethyl)ether Bis(2-chloroisopropyl)ether 4-Bromophenyl phenyl ether	Benzotrichloride 2-Chloronaphthalene 1,2-Dichlorobenzene 1,3-Dichlorobenzene 1,4-Dichlorobenzene Hexachlorobenzene Hexachlorobutadiene α-HCH [α-BHC] -HCH [-BHC] -HCH [-BHC] -HCH [-BHC, Lindane] Hexachlorocyclopentadiene Hexachloroethane Pentachlorobenzene 1,2,4,5-Tetrachlorobenzene 1,2,4-Trichlorobenzene	Aniline 4-Chloroaniline 2-Nitroaniline 3-Nitroaniline 4-Nitroaniline **Not all 8270 aniline derivatives are listed as 8131 analytes.*	Demeton-O Demeton-S Dichlorvos Dimethoate Disulfoton Ethion Malathion Naled Parathion Phorate Phosmet Terbufos	**Benzo[a]anthracene** **Benzo[a]pyrene** **Benzo[b]fluoranthene** **Benzo[k]fluoranthene** **Chrysene** **Dibenzo[a,h]anthracene** **Indeno[1,2,3-cd]pyrene** ***RISC* cPAHs** (Chemicals of Concern for: Hydrocarbon Oils and High-end Liquid Hydrocarbon Fuels) Acenaphthene Acenaphthylene Benzo[g,h,i]perylene Chrysene Fluoranthene Fluorene Naphthalene Phenanthrene Pyrene **N-Methylcarbamates** Method 8318- Carbaryl Carbofuran

Chemical classes commonly encountered in environmental projects are illustrated in the following table:

Chemical Classes in Organic Analyses
Chemical Classes by Method

Volatile Compounds (GC/MS Method 8260)	Semivolatile Compounds (GC/MS Method 8270)
•Nonhalogenated compounds (GC/FID Method 8015) (*compounds <u>not</u> containing <u>halogens</u> (i.e.,Cl, Br, F, I)*) •Halogenated compounds (GC/PID Method 8021) *(compounds containing Cl, Br, F, or I)* •Aromatic compounds (GC/PID Method 8021) *(Benzene derivatives - **includes BTEX**)*	•Phenol compounds (GC/FID-ECD Method 8041) *(e.g., pentachlorophenol, 2,4-dimethylphenol)* •Phthalate esters (GC/ECD Method 8061) *(plasticizers, e.g. di-n-octyl phthalate)* •Organochlorine pesticides (GC/ECD Method 8081) *(e.g, Lindane, DDT, Endrin)* •Polychlorinated biphenyls (PCBs) (GC/ECD 8082) *(e.g. Aroclor 1248, 2-chlorobiphenyl)* •Nitroaromatics and Cyclic ketones (GC/ECD 8091) *(E.g, 1,2-dinitrobenzene, 1,4-naphthoquinone)* •Haloethers (GC/ECD Method 8111) *(ethers containing halogens, e.g., bis(2-chloroethyl)ether)* •Chlorinated Hydrocarbons (GC/ECD Method 8121) *(hydrocarbon solvents and pesticides containing chlorine)* •Aniline and derivatives (GC/NPD Method 8131) *(aminobenzene and derivatives)* •Organophosphorous Compounds (GC/NPD 8141) *(Pesticides containing phosphorus, e.g., malathion)* •Polynuclear Aromatic Hydrocarbons (HPLC 8310) *(Coal tar/creosote/petroleum components; **includes cPAHs)***


You have
Just left a
Critical
Area
WARNING!
Critical Area
Re-entry
May be required!
QAPP
Revision for
DQO
Clarification
Ahead

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PART IV.

Quality Assurance/Quality Control Principles
and
QAPP Preparation

PART IV.[15]

Quality Assurance/Quality Control Principles and QAPP Preparation

1.0 INTRODUCTION

It is the goal of the Indiana Department of Environmental Management (IDEM) to ensure that data be defensible, scientifically valid, and of known precision and accuracy.. The data must be of sufficient known quality to withstand scientific and legal challenge relative to the use for which the data are obtained. The Quality System, incorporating Quality Assurance/Quality Control (QA/QC) principles, is the facility's tool for achieving this goal.

For IDEM analyses related to closure, cleanup, and waste characterization, the minimum requirements for a QA program and associated QC procedures are provided in this Part.

The data acquired from QC procedures are used to estimate the quality of analytical data, to determine the need for corrective action in response to identified deficiencies, and to interpret results after corrective action procedures are implemented. Method-specific QC procedures are incorporated in the individual methods, since they are not applied universally.

A total program to generate data of acceptable quality should include both a QA component, which encompasses the management procedures and controls, as well as an operational day-to-day QC component. This Part defines fundamental elements of such a data collection program. Data collection efforts involve:

1. design of a Quality Assurance Project Plan (QAPP) to achieve the data quality objectives (DQOs);

2. implementation of the QAPP; and

3. assessment of the data to determine if the DQOs are met.

This Part identifies the QC components to be used in the performance of sampling and analyses, including the QC information which is to be documented (i.e., QA). Guidance is provided to construct QA programs for field and laboratory work conducted in support of the environmental projects for IDEM programs.

2.0 QA PROJECT PLAN

All projects which generate environment related data in support of IDEM programs require a Quality Assurance Project Plan or equivalent. In some instances, a sampling and analysis plan or a waste analysis plan may be equivalent if it includes all necessary information and may be substituted.

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[15]Adapted from *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*, U.S. EPA Publication SW-846, Chapter One (Rev. 1), "Quality Control," 3rd ed., *Final Update I*, July, 1992.

The QAPP should detail the DQOs and QA/QC goals and protocols for a specific data collection activity. It sets forth the sampling and analysis activities that will generate data of a quality commensurate with their intended use. The QAPP elements should include: a description of the project and its objectives; a statement of the DQOs of the project; identification of those involved in the data collection and their responsibilities and authorities; reference to (or inclusion of) the specific sample collection and analysis procedures that will be followed for all aspects of the project; enumeration of QC procedures to be followed; and descriptions of all project documentation. Additional elements may be included in the plan if needed to address all quality related aspects of the data collection project. Elements may be omitted when inappropriate or inconsequential to the project (see reference 1).

The role and importance of DQOs and project documentation are discussed below in Sections 2.1 through 2.6. Management and organization play a critical role in determining the effectiveness of a plan and ensuring that all required procedures are followed. Section 2.7 discusses the elements of an organization's QA. Field operations and laboratory operations (along with applicable QC procedures) are discussed in Sections 3, and 4, respectively.

2.1 Data Quality Objectives

Data quality objectives for the data collection activity describe the overall level of uncertainty that a decision-maker is willing to accept in results derived from environmental data. This uncertainty is used to specify the quality of the measurement data required, usually in terms of objectives for precision, bias, representativeness, comparability and completeness. The DQOs should be defined prior to the initiation of the field and laboratory work. The field and laboratory organizations performing the work should be aware of the DQOs so that their personnel may make informed decisions during the course of the project to attain those DQOs. More detailed information on DQOs is available from the U.S. EPA Quality Assurance Management Staff (QAMS) (see references 2 and 4).

2.2 Project Objectives

A statement of the project objectives and how the objectives are to be attained is to be concisely stated and sufficiently detailed to permit clear understanding by all parties involved in the data collection effort. This includes a statement of what problem is to be solved and the information required in the process. It also includes appropriate statements of the DQOs (i.e., the acceptable level of uncertainty in the information).

2.3 Sample Collection

Sampling procedures[16], locations, equipment, and sample preservation and handling requirements are to be specified in the plan. Further details on the procedures for field operations are described in Section 3 of this Part. Specific procedures for groundwater sampling are provided in Chapter Eleven of SW-846.

2.4 Analysis and Testing

Analytes and properties of concern, analytical and testing procedures to be employed, required detection limits, and requirements for precision and bias are to be specified. All applicable regulatory requirements and the project DQOs should be considered when developing the specifications. Further details on the procedures for analytical operations are described in Section 4 of this Part and Part V.

[16]Note: When there is a separate SAP, care should be taken to ensure there is consistency of sampling procedures in the QAPP and SAP.

2.5 Quality Control

The quality assurance program should address both field and laboratory activities. Quality control procedures are to be specified for estimating the precision and bias of the data. Recommended minimum requirements for QC samples have been established by EPA and IDEM and should be met in order to satisfy minimum criteria for acceptable data quality. Further details on procedures for field and laboratory operations are described in Sections 3 and 4, respectively, of this Part and Part V.

2.6 Project Documentation

Documents are to be prepared and maintained in conjunction with the data collection effort. Project documentation should be sufficient to allow review of all aspects of the work being performed. The QAPP discussed in Sections 3.6 and 4.6 is an important document that is to be maintained.

The length of storage time for project records should comply with regulatory requirements, organizational policy, or project requirements, whichever is more stringent. At a minimum, documentation should be stored for three years from submission of the project final report.

Documentation is to be secured in a facility that minimizes its deterioration for the length of time that it is to be retained. A system allowing for the expedient retrieval of information should exist.

Access to archived information should be controlled to maintain the integrity of the data. All access to archive information should be documented. This documentation should include the name of the individual, the date, the reason for accessing the data, and all changes, deletions, or withdrawals that may have occurred.

2.7 Organization Performing Field or Laboratory Operations

Proper design and structure of the organization facilitates effective and efficient transfer of information and helps to prevent required procedures from being overlooked.

The organizational structure, functional responsibilities, levels of authority, job descriptions, and lines of communication for all project activities should be established and documented. One person may cover more than one organizational function. Each project participant should have a clear understanding of his duties and responsibilities and the relationship of those responsibilities to the overall data collection effort.

The management of each organization participating in a project involving data collection activities should establish that organization's operational and QA policies. This information should be documented in the QAPP. The management should ensure that (1) the appropriate methodologies are followed as documented in the QAPP; (2) personnel clearly understand their duties and responsibilities; (3) each staff member has access to appropriate project documents; (4) any deviations from the QAPP are communicated to the project management and documented; and (5) communication occurs between the field, laboratory, and project management, as specified in the QAPP.

The management of the participating field or laboratory organization should establish personnel qualifications and training requirements for the project. Each person participating in the project should have the education, training, technical knowledge, and experience, or a combination thereof, to enable that individual to perform assigned functions. Training should be provided for each staff member as necessary

to perform functions properly. Personnel qualifications should be documented in terms of education, experience, and training, and periodically reviewed to ensure adequacy to current responsibilities.

Each participating field organization or laboratory organization should have a designated QA function (i.e., a team or individual trained in QA) to monitor operations to ensure that the equipment, personnel, activities, procedures, and documentation conform with the QAPP. To the extent possible, the QA monitoring function should be entirely separate from, and independent of, personnel engaged in the work being monitored. The QA function should be responsible for the QA review.

2.7.1 Performance Evaluation

Performance evaluation studies are used to measure the performance of the laboratory on unknown samples. Performance evaluation samples are typically submitted to the laboratory as blind samples by an independent outside source. The results are compared to predetermined acceptance limits. Performance evaluation samples can also be submitted to the laboratory as part of the QA function during internal assessment of laboratory performance. Records of all performance evaluation studies should be maintained by the laboratory. Problems identified through participation in performance evaluation studies should be immediately investigated and corrected.

2.7.2 Internal Assessment by QA Function

Personnel performing field and laboratory activities are responsible for continually monitoring individual compliance with the QAPP. The QA function should review procedures, results and calculations to determine compliance with the QAPP. The results for this internal assessment should be reported to management with requirements for a plan to correct observed deficiencies.

2.7.3 External Assessment

The field and laboratory activities may be reviewed by personnel external to the organization. Such an assessment is an extremely valuable method for identifying overlooked problems. The results of the external assessment should be submitted to management with requirements for a plan to correct observed deficiencies.

2.7.4 On-Site Evaluation

On-site evaluations may be conducted as part of both internal and external assessments. The focus of an on-site evaluation is to evaluate the degree of conformance of project activities with the applicable QAPP. On-site evaluations may include, but are not limited to, a complete review of facilities, staff, training, instrumentation, procedures, methods, sample collection, analyses, QA policies and procedures related to the generation of environmental data. Records of each evaluation should include the date of the evaluation, location, the areas reviewed, the person performing the evaluation, findings and problems, and actions recommended and taken to resolve problems. Any problems identified that are likely to affect data integrity should be brought immediately to the attention of management.

2.7.4.1 Field Activities

The review of field activities should be conducted by one or more persons knowledgeable in the activities being reviewed, evaluating at a minimum the following subjects:

Completeness of Field Reports -- This review determines whether all requirements for field activities in the QAPP have been fulfilled, that complete records exist for each field activity, and that the procedures specified in the QAPP have been implemented. Emphasis on field documentation will help assure sample integrity and sufficient technical information to recreate each field event. The results of this completeness check should be documented, and environmental data affected by incomplete records should be identified.

Identification of Valid Samples -- This review involves interpretation and evaluation of the field records to detect problems affecting the representativeness of environmental samples. Examples of items that might indicate potentially invalid samples include improper well development, improperly screened wells, instability of pH or conductivity, and collection of volatiles near internal combustion engines. The field records should be evaluated against the QAPP and SOPs. The reviewer should document the sample validity and identify the environmental data associated with any poor or incorrect field work.

Correlation of Field Test Data -- This review involves comparing any available results of field measurements obtained by more than one method. For example, surface geophysics may be surveyed using both ground penetrating radar and a resistivity survey.

Identification of Anomalous Field Test Data -- This review identifies any anomalous field test data. For example, a water temperature for one well that is 5 degrees higher than any other well temperature in the same aquifer should be noted. The reviewer should evaluate the impact of anomalous field measurement results on the associated environmental data.

Validation of Field Analyses -- This review validates and documents all data from field analysis that are generated in situ or from a mobile laboratory as specified in Section 2.7.4.2. The reviewer should document whether the QC checks meet the acceptance criteria, and whether corrective actions were taken for any analysis performed when acceptance criteria were exceeded.

2.7.4.2 Laboratory Activities

The evaluation of laboratory data should be conducted by one or more persons knowledgeable in laboratory activities, evaluating at a minimum, the following subjects:

Completeness of Laboratory Records -- This review determines whether: (1) all samples and analyses required by the QAPP have been processed, (2) complete records exist for each analysis and the associated QC samples, and that (3) the procedures specified in the QAPP have been implemented. The results of the completeness check should be documented, and environmental data affected by incomplete records should be identified.

Evaluation of Data with Respect to Detection Limits -- This review compares analytical results to required detection limits and documents any detection limits that exceed regulatory limits or action levels, as specified in the QAPP.

Evaluation of Data with Respect to Control Limits -- This review compares the results of QC and calibration check samples to control criteria. Data not within control limits require corrective action, and the reviewer should check that corrective action reports, and the results of reanalysis, are available.

The review should determine if samples associated with out-of-control QC data are identified in a written record of the data review, and if an assessment of the utility of such analytical results is recorded.

Review of Holding Time Data -- This review compares sample holding times to those required by the QAPP, and notes all deviations.

Review of Performance Evaluation (PE) Results -- PE results can be helpful in evaluating the impact of out-of-control conditions. This review documents any recurring trends or problems evident in PE studies and evaluates their effect on environmental data.

Correlation of Laboratory Data -- This review determines if the results of data obtained from related laboratory tests, (e.g., Purgeable Organic Halides (POX), and Volatile Organics) are documented, and whether the significance of any differences is discussed in the reports. Additional guidelines and specific control criteria are provided in (Part V, Laboratory Analytical Guidelines).

2.7.5 QA Reports

There should be periodic reporting of pertinent QA/QC information to the project management to allow assessment of the overall effectiveness of the QA program. There are three major types of QA reports to project management:

Periodic Report on Key QA Activities -- This provides a summary of key QA activities during the period, stressing measures that are being taken to improve data quality; describes significant quality problems observed and corrective actions taken; reports information regarding any changes in certification/accreditation status; describes involvement in resolution of quality issues with clients or agencies; reports any QA organizational changes; and provides notice of the distribution of revised documents controlled by the QA organization (i.e., procedures).

Report on Measurement Quality Indicators -- This includes the assessment of QC data gathered over the period, the frequency of analyses repeated due to unacceptable QC performance, and, if possible, the reason for the unacceptable performance and corrective action taken.

Reports on QA Assessments -- This Includes the results of the assessments and the plan for correcting identified deficiencies and should be submitted immediately following any internal or external on-site evaluation or upon receipt of the results of any performance evaluation studies. This also includes results of the assessments and the plan for correcting identified deficiencies.

3.0 FIELD OPERATIONS

The field operations must be conducted in such a way as to provide reliable information that meets the DQOs. To achieve this, certain minimal policies and procedures must be implemented. Supplemental information and guidance is available in the RCRA Ground-Water Monitoring Technical Enforcement Guidance Document (TEGD) (Reference 3). The project documentation should contain the information specified below.

3.1 Field Logistics

The proper accomplishment of this activity should not be overlooked. Ineffectual sampling negates the accomplishment of laboratory analyses. The QAPP should describe the type(s) of field operations to be performed and the appropriate area(s) in which to perform the work. The QAPP should address ventilation, protection from extreme weather and temperatures, access to stable power, and provision for water and gases of required purity.

Whenever practical, the sampling site facilities should be examined prior to the start of work to ensure that all required items are available, The actual area of sampling should be examined to ensure that trucks, drilling equipment, and personnel have adequate access to the site.

The determination as to whether sample shipping is necessary should be made during planning for the project. This need is established by evaluating the analyses required, sample holding times, and location of the site and the laboratory. Shipping or transporting of samples to a laboratory must be done within a time-frame such that recommended holding times are met.

Samples should be packaged, labeled, preserved (e.g., preservative added, iced, etc.) and documented in an area which is free of contamination and provides for secure storage. The type of custody and whether sample storage is needed should be addressed in the QAPP.

Storage areas for solvents, reagents, standards, and reference materials should be adequate to preserve their identity, concentration, purity, and stability prior to use.

Decontamination of sampling equipment may be performed at the location where sampling occurs, prior to going to the sampling site, or in designated areas near the sampling site. Project documentation should specify where and how this work is accomplished. If decontamination is to be done at the site, water and solvents of appropriate purity should be available. The method of accomplishing decontamination, including the required materials, solvents, and water purity should be specified.

During the sampling process and during on-site or in situ analyses, waste materials are sometimes generated. The method for storage and disposal of these waste materials should be specified. Adequate facilities should be provided for the collection and storage of all wastes, and these facilities should be operated so as to minimize environmental contamination. Waste storage and disposal facilities should comply with applicable federal, state, and local regulations. The location of long-term and short-term storage for field records, and the measures to ensure the integrity of the data should be specified.

3.2 Equipment/Instrumentation

The equipment, instrumentation, and supplies at the sampling site should be specified and must be appropriate to accomplish the activities planned. The equipment and instrumentation should meet the requirements of specifications, methods, and procedures as specified in the QAPP.

3.3 Operating Procedures

The QAPP should describe or make reference to all field activities that may affect data quality. For routinely performed activities, standard operating procedures (SOPs) are often prepared to ensure consistency and to save time and effort in preparing QAPPs. Any deviation from an established procedure during a data collection activity should be documented. The procedures should be available for the indicated activities, and should include, at a minimum, the information described below.

3.3.1 Sample Management

The numbering and labeling system, chain-of-custody procedures, and how the samples are to be tracked from collection to shipment or receipt by the laboratory should be specified. Sample management procedures should also specify the holding times, volumes of sample required by the laboratory, required preservatives, and shipping requirements.

3.3.2 Reagent/Standard Preparation

The procedures describing how to prepare standards and reagents should be specified. Information concerning specific grades of materials used in reagent and standard preparation, appropriate glassware and containers for preparation and storage, and labeling and record keeping for stocks and dilutions should be included.

3.3.3 Decontamination

The procedures describing decontamination of field equipment before and during the sample collection process should be specified. These procedures should include cleaning materials used, the order of washing and rinsing with the cleaning materials, requirements for protecting or covering cleaned equipment, procedures for verifying the cleaning of equipment, and procedures for disposing of cleaning materials.

3.3.4 Sample Collection

The procedures describing how the sampling operations are actually performed in the field should be specified. A simple reference to standard methods is not sufficient, unless a procedure is performed exactly as described in the published method.

Methods from source documents published by the EPA, American Society for Testing and Materials, U.S. Department of the Interior, National Water Well Association, American Petroleum Institute, or other recognized organizations with appropriate expertise should be used, if possible. The procedures for sample collection should include at least the following:

- Applicability of the procedure,

- Equipment required,
- Detailed description of procedures to be followed in collecting the samples,
- Common problems encountered and corrective actions to be followed, and
- Precautions to be taken.

3.3.5 Field Measurements

The procedures describing all methods used in the field to determine a chemical or physical parameter should be described in detail. The procedures should address criteria from Section 4, as appropriate.

3.3.6 Equipment Calibration And Maintenance

The procedures describing how to ensure that field equipment and instrumentation are in working order are to be specified. These describe calibration procedures and schedules, maintenance procedures and schedules, maintenance logs, and service arrangements for equipment. Calibration and maintenance of field equipment and instrumentation should be in accordance with manufacturers' specifications or applicable test specifications and should be documented.

3.3.7 Corrective Action

The procedures describing how to identify and correct deficiencies in the sample collection process should be specified. These should include specific steps to take in correcting deficiencies such as performing additional decontamination of equipment, re-sampling, or additional training of field personnel. The procedures should specify that each corrective action must be documented with a description of the deficiency and the corrective action taken, and should include the person(s) responsible for implementing the corrective action.

3.3.8 Data Reduction and Validation

The procedures describing how to compute results from field measurements and to review and validate these data are to be specified. They are to include all formulas used to calculate results and procedures to independently verify that field measurement results are correct.

3.3.9 Reporting

The procedures describing the process for reporting the results of field activities are to be specified.

3.3.10 Records Management

The procedures describing the means for generating, controlling, and archiving project-specific records and field operations records should be specified. These procedures should detail record generation and control, and the requirements for record retention, including type, time, security, and retrieval and disposal authorities.

Project-specific records -- These relate to field work performed for a project. These records may include correspondence, chain-of-custody records, field notes, all reports issued as a result of the work, and procedures used.

Field operations records -- These document overall field operations and may include equipment performance and maintenance logs, personnel files, general field procedures, and corrective action reports.

3.3.11 Waste Disposal

The procedures describing the methods for disposal of waste materials resulting from field operations should be specified.

3.4 Field QA and QC Requirements

The QAPP or relevant plan describe how the following required elements of the field QC program should be implemented.

3.4.1 Control Samples

Control samples are QC samples that are introduced into a process to monitor the performance of the system. Control samples, which may include blanks, duplicates, spikes, analytical standards, and reference materials, can be used in different phases of the data collection process beginning with sampling and continuing through transportation, storage, and analysis.

For each sampling batch, when appropriate for the sampling method, at least one field duplicate per matrix type, and one equipment rinsate is to be collected. When samples are collected for volatile organic analysis, a trip blank is also required for each day that samples are collected.

In addition, for each batch, collect enough volume for at least one sample per matrix type to allow the laboratory to prepare one matrix spike and either one matrix duplicate or one matrix spike duplicate per analytical batch when appropriate for the method. Additional control samples may be necessary in order to assure data quality to meet the project-specific DQOs.

3.4.2 Acceptance Criteria

Procedures should be in place for establishing acceptance criteria for field activities described in the QAPP. Acceptance criteria may be qualitative or quantitative. Field events or data that fall outside of established acceptance criteria may indicate a problem with the sampling process that should be investigated.

3.4.3 Deviations

All deviations from planned events are to be documented as to the extent of, and reason for, the deviation. Any activity not performed in accordance with procedures or QAPPs is considered a deviation from plan. Deviations from plan may or may not affect data quality.

3.4.4 Corrective Action

Errors, deficiencies, deviations, certain field events, or data that fall outside established acceptance criteria require investigation. In some instances, corrective action may be needed to resolve the problem and restore proper functioning to the system. The investigation of the problem and any subsequent corrective action taken should be documented.

3.4.5 Data Handling

All field measurement data should be reduced according to protocols described or referenced in the QAPP. Computer programs used for data reduction should be validated before use and verified on a regular basis. All information used in the calculations is to be recorded to enable reconstruction of the final result at a later date.

Data should be reported in accordance with the requirements of the end-user as described in the QAPP.

3.5 Quality Assurance Review

The QA Review consists of internal and external assessments to ensure that QA/QC procedures are in use and to ensure that field staff conform to these procedures. The QAPP should specify the requirements for internal, external, and on-site assessment, including the frequency and documentation of these assessments.

3.6 Field Records

Records provide the direct evidence and support for the necessary technical interpretations, judgements, and discussions concerning project activities. These records, particularly those that are anticipated to be used as evidentiary data, should directly support current or ongoing technical studies and activities and should provide the historical evidence needed for later reviews and analyses. Records should be legible, identifiable, and retrievable and protected against damage, deterioration, or loss.

Field records generally consist of bound field notebooks with pre-numbered pages, sample collection forms, personnel qualification and training forms, sample location maps, equipment maintenance and calibration forms, chain-of-custody forms, sample analysis request forms, and field change request forms. All records should be written in indelible ink.

Procedures for reviewing, approving, and revising field records should be clearly defined, with the lines of authority included. At a minimum, all documentation errors should be corrected by drawing a single line through the error so it remains legible and should be initialed by the responsible individual, along with the date of change. The correction should be written adjacent to the error.

Field records should include (but are not limited to) the following:

Calibration Records & Traceability of Standards/Reagents -- Calibration is a reproducible reference point to which all sample measurements can be correlated. A sound calibration program should include

provisions for documentation of frequency, conditions, standards, and records reflecting the calibration history of a measurement system. The accuracy of the calibration standards is important because all data will be in reference to the standards used. A program for verifying and documenting the accuracy of all working standards against primary grade standards should be routinely followed.

Sample Collection -- To ensure maximum utility of the sampling effort and resulting data, documentation of the sampling protocol, as performed in the field, is essential. Sample collection records should contain, at a minimum, the names of persons conducting the activity, sample number, sample location, equipment used, climatic conditions, documentation of adherence to protocol, and unusual observations. The actual sample collection record is usually one of the following: a bound field notebook with pre-numbered pages, a pre-printed form, or digitized information on a computer tape or disk.

Chain-of-Custody Records -- The chain-of-custody involving the possession of samples from the time they are obtained until they are disposed or shipped off-site should be documented as specified in the QAPP and should include the following information: (1) the project name; (2) signatures of samplers; (3) the sample number, date and time of collection, and grab or composite sample designation; (4) signatures of individuals involved in sample transfer; and (5) if applicable, the air bill or other shipping number.

Maps and Drawings -- Project planning documents and reports often contain maps. The maps are used to document the location of sample collection points and monitoring wells and as a means of presenting environmental data. Information used to prepare maps and drawings is normally obtained through field surveys, property surveys, surveys of monitoring wells, aerial photography or photogrammetric mapping. The final approved maps and/or drawings should have a revision number and date and should be subject to the same controls as other project records.

QC Samples -- Documentation for generation of QC samples, such as trip and equipment rinsate blanks, duplicate samples, and any field spikes should be maintained.

Deviations -- All deviations from procedures, documents, and the QAPP should be recorded in the site logbook.

Reports -- A copy of any report issued and any supporting documentation should be retained.

4.0 LABORATORY OPERATIONS

The laboratory should conduct its operations in such a way as to provide reliable information. To achieve this, certain minimal policies and procedures should be implemented.

4.1 Facilities

The QAPP should address all facility-related issues that may impact project data quality. Each laboratory should be of suitable size and construction to facilitate the proper conduct of the analyses. Adequate bench space or working area per analyst should be provided. The space requirement per analyst depends on the equipment or apparatus that is being utilized, the number of samples that the analyst is expected to handle

at any one time, and the number of operations that are to be performed concurrently by a single analyst. Other issues to be considered include, but are not limited to, ventilation, lighting, control of dust and drafts, protection from extreme temperatures, and access to a source of stable power.

Laboratories should be designed so that there is adequate separation of functions to ensure that no laboratory activity has an adverse effect on the analyses. The laboratory may require specialized facilities such as a perchloric acid hood or glove-box.

Separate space for laboratory operations and appropriate ancillary support should be provided, as needed, for the performance of routine and specialized procedures.

As necessary to ensure secure storage and prevent contamination or misidentification, there should be adequate facilities for receipt and storage of samples. The level of custody required and any special requirements for storage such as refrigeration should be described in planning documents.

Storage areas for reagents, solvents, standards, and reference materials should be adequate to preserve their identity, concentration, purity, and stability.

Adequate facilities should be provided for the collection and storage of all wastes, and these facilities should be operated so as to minimize environmental contamination. Waste storage and disposal facilities should comply with applicable federal, state, and local regulations.

The location of long-term and short-term storage of laboratory records and the measures to ensure the integrity of the data should be specified.

4.2 Equipment and Instrumentation

Equipment and instrumentation should meet the requirements and specifications of the specific test methods and other procedures as specified in the QAPP. The laboratory should maintain an equipment/instrument description list that includes the manufacturer, model number, year of purchase, accessories, and any modifications, updates, or upgrades that have been made.

4.3 Operating Procedures

The QAPP should describe or make reference to all laboratory activities that may affect data quality. For routinely performed activities, SOPs are often prepared and used to ensure consistency and to save time and effort in preparing QAPPs. Any deviation from an established procedure during a data collection activity must be documented. The procedures should be available for the indicated activities, and should include, at a minimum, the information described below.

4.3.1 Sample Management

The procedures describing the receipt, handling, scheduling, and storage of samples should be specified.

Sample Receipt and Handling -- These procedures describe the precautions to be used in opening sample shipment containers and how to verify that chain-of-custody has been maintained, examine samples for damage, check for proper preservatives and temperature, and log samples into the

laboratory sample streams.

Sample Scheduling -- These procedures describe the sample scheduling in the laboratory and include procedures used to ensure that holding time requirements are met.

Sample Storage -- These procedures describe the storage conditions for all samples, verification and documentation of daily storage temperature, and how to ensure that custody of the samples is maintained while in the laboratory.

4.3.2 Reagent/Standard Preparation

The procedures describing how to prepare standards and reagents are to be specified. Information concerning specific grades of materials used in reagent and standard preparation, appropriate glassware and containers for preparation and storage, and labeling and record-keeping for stocks and dilutions should be included.

4.3.3 General Laboratory Techniques

The procedures describing all essentials of laboratory operations that are not addressed elsewhere should be specified. These techniques should include, but are not limited to, glassware cleaning procedures, operation of analytical balances, pipetting techniques, and use of volumetric glassware.

4.3.4 Test Methods

Procedures for test methods describing how the analyses are actually performed in the laboratory should be specified. A simple reference to standard methods is not sufficient, unless the analysis is performed exactly as described in the published method. Whenever methods from SW-846 are not appropriate, recognized methods from source documents published by the EPA, American Public Health Association (APHA), American Society for Testing and Materials (ASTM), the National Institute for Occupational Safety and Health (NIOSH), or other recognized organizations with appropriate expertise should be used, if possible. The documentation of the actual laboratory procedures for analytical methods should include the following:

Sample Preparation and Analysis Procedures -- These include applicable holding time, extraction, digestion, or preparation steps as appropriate to the method; procedures for determining the appropriate dilution to analyze; and any other information required to perform the analysis accurately and consistently.

Instrument Standardization -- This includes concentration(s) and frequency of analysis of calibration standards, linear range of the method, and calibration acceptance criteria.

Sample Data -- This includes recording requirements and documentation including sample identification number, analyst, data verification, date of analysis and verification, and computational method(s).

Precision and Bias -- This includes all analyses for which the method is applicable and the conditions for use of this information.

Detection and Reporting Limits -- This includes all analyses in the method.

Test-Specific QC -- This describes QC activities applicable to the specific test and references any applicable QC procedures.

4.3.5 Equipment Calibration and Maintenance

The procedures describing how to ensure that laboratory equipment and instrumentation are in working order should be specified. These procedures include calibration procedures and schedules, maintenance procedures and schedules, maintenance logs, service arrangements for all equipment, and spare parts available in-house. Calibration and maintenance of laboratory equipment and instrumentation should be in accordance with manufacturers' specifications or applicable test specifications and should be documented. Additional specific guidelines are provided in Part V.

4.3.6 QC

The type, purpose, and frequency of QC samples to be analyzed in the laboratory and the acceptance criteria should be specified. Information should include the applicability of the QA sample to the analytical process, the statistical treatment of the data, and the responsibility of laboratory staff and management in generating and using the data. Further details on development of project-specific QC protocols are described in Section 4.4.

4.3.7 Corrective Action

The procedures describing how to identify and correct deficiencies in the analytical process should be specified. These should include specific steps to take in correcting the deficiencies such as preparation of new standards and reagents, re-calibration and re-standardization of equipment, reanalysis of samples, or additional training of laboratory personnel in methods and procedures. The procedures should specify that each corrective action must be documented with a description of the deficiency and the corrective action taken, and should include the person(s) responsible for implementing the corrective action.

4.3.8 Data Reduction and Validation

The procedures describing how to review and validate the data should be specified. They should include procedures for computing and interpreting the results from QC samples, and independent procedures to verify that the analytical results are reported correctly. In addition, routine procedures used to monitor precision and bias, including evaluations of reagent equipment rinsate, trip blanks, method blanks, calibration standards, control samples, duplicate and matrix spike samples, and surrogate recovery, should be detailed in the procedures.

4.3.9 Reporting

All analytical reports should be formatted to contain the parameter names in the order given on the appropriate sample reporting forms per analyte, analytical result obtained or detection level if not detected, laboratory sample identification, the sample number or identification number assigned by the requestor, dates of sample prep and analysis for each parameter, and all required Quality Assurance/Quality Control information described by QA/QC measures. (See Appendix II for additional information.)

4.3.10 Records Management

The procedures describing the means for generating, controlling, and archiving laboratory records should be specified. The procedures should detail record generation and control, and the requirements for record retention, including type, time, security, and retrieval and disposal authorities.

Project-specific records -- These may include correspondence, chain-of-custody records, request for analysis, calibration data records, raw and finished analytical and QC data, data reports, and procedures used.
Laboratory operations records -- These may include laboratory notebooks, instrument performance logs and maintenance logs in bound notebooks with pre-numbered pages, laboratory bench-sheets, software documentation, control charts, reference material certification, personnel files, laboratory procedures, and corrective action reports.

4.3.11 Waste Disposal

The procedures describing the methods for disposal of chemicals, including standard and reagent solutions, process waste, and samples, should be specified.

4.4 Laboratory QA and QC Requirements

The QAPP should describe how the following required elements of the laboratory QC program are to be implemented.

4.4.1 Method Proficiency

Procedures should be in place for demonstrating proficiency with each analytical method routinely used in the laboratory. These should include procedures for demonstrating the precision and bias of the method as performed by the laboratory and procedures for determining the method detection limit (MDL). All terminology, procedures and frequency of determinations associated with the laboratory's establishment of the MDL and the reporting limit should be well-defined and well-documented. Documented precision, bias, and MDL information should be maintained for all methods performed in the laboratory.

4.4.2 Control Limits

Procedures should be in place for establishing and updating control limits for analysis. Control limits should be established to evaluate laboratory precision and bias based on the analysis of control samples. Typically, control limits for bias are based on the historical mean recovery plus or minus three standard deviation units, and control limits for precision range from zero (no difference between duplicate control samples) to the historical mean relative percent difference plus three standard deviation units. Procedures should be in place for monitoring historical performance and should include graphical (control charts) and/or tabular presentations of the data.

4.4.3 Laboratory Control Procedures

Procedures should be in place for demonstrating that the laboratory is in control during each data collection activity. Analytical data generated with laboratory control samples that fall within prescribed limits are judged to be generated while the laboratory was in control. Data generated with laboratory control samples that fall outside the established control limits are judged to be generated during an "out-of-control" situation. These data are considered suspect and must be repeated or reported with qualifiers. Additional specific guidance is provided in Part V.

Laboratory Control Samples -- Laboratory control samples should be analyzed for each analytical method when appropriate for the method. A laboratory control sample consists of either a control matrix spiked with analytes representative of the target analytes or a certified reference material. Laboratory control sample(s) should be analyzed with each batch of samples processed to verify that the precision and bias of the analytical process are within control limits. The results of the laboratory control sample(s) are compared to control limits established for both precision and bias to determine usability of the data.

Method Blank -- When appropriate for the method, a method blank should be analyzed with each batch of samples processed to assess contamination levels in the laboratory. Guidelines should be in place for accepting or rejecting data based on the level of contamination in the blank.

Procedures should be in place for documenting the effect of the matrix on method performance. When appropriate for the method, there should be at least one matrix spike and either one matrix duplicate or one matrix spike duplicate per analytical batch. Additional control samples may be necessary to assure data quality to meet the project-specific DQOs.

Matrix-Specific Bias -- Procedures should be in place for determining the bias of the method due to the matrix. These procedures should include preparation and analysis of matrix spikes, selection and use of surrogates for organic methods, and the method of standard additions for metal and inorganic methods. When the concentration of the analyte in the sample is greater than 0.1%, the spiked of the analyte may not be necessary.

Matrix-Specific Precision -- Procedures should be in place for determining the precision of the method for the matrix. These procedures should include analysis of matrix duplicates and/or matrix spike duplicates. The frequency of use of these techniques should be based on the DQO for the data collection activity.

Matrix-Specific Detection Limit -- Procedures should be in place for determining the MDL for a specific matrix type (e.g., waste-water treatment sludge, contaminated soil, etc).

4.4.4 Deviations

Any activity not performed in accordance with laboratory procedures or QAPPs is considered a deviation from plan. All deviations from the plan are to be documented as to the extent of, and reason for, the deviation.

4.4.5 Corrective Action

Errors, deficiencies, deviations, or laboratory events or data that fall outside of established

acceptance criteria require investigation. In some instances, corrective action may be needed to resolve the problem and restore proper functioning to the analytical system. The investigation of the problem and any subsequent corrective action taken require documentation.

4.4.6 Data Handling

Data resulting from the analyses of samples should be reduced according to protocols described in the laboratory procedures. Computer programs used for data reduction should be validated before use and verified on a regular basis. All information used in the calculations should be recorded in order to enable reconstruction of the final result at a later date. This information may include weight or volume of sample used, percent dry weight for solids, extract volume, dilution factor used, and background-correction protocols followed.

All data should be reviewed by a second analyst or supervisor according to laboratory procedures to ensue that calculations are correct and to detect transcription errors. Spot checks should be performed on computer calculations to verify program validity. Errors detected in the review process should be referred to the analyst(s) for corrective action. Data should be reported in accordance with the requirements of the end user. The supporting documentation should include as a minimum:

- Laboratory Name and Address.
- Sample information (including unique sample identification, sample collection date and time, date of sample receipt, and date(s) of sample preparation and analysis).
- Analytical results reported with appropriate significant figures.
- Detection limits that reflect dilutions, interferences, or correction for equivalent dry weight.
- Method reference.
- Appropriate QC results (correlation with sample batch should be traceable and documented).
- Data qualifiers with appropriate references and narrative on the quality of the results.

4.5 Quality Assurance Review

The QA review consists of internal and external assessments to ensure that QA/QC procedures are in use and to ensure that laboratory staff conform to these procedures. The QAPP should specify the requirements for internal, external, and on-site assessments, including the frequency and documentation of these assessments.

4.6 Laboratory Records

Records provide the direct evidence and support for the necessary technical interpretations, judgements and discussions concerning project activities. These records, particularly those that are anticipated to be used as evidentiary data, must directly support technical studies and activities, and provide the historical evidence needed for later reviews and analyses. Records should be legible, identifiable, and retrievable, and protected against damage, deterioration, or loss.

Laboratory records generally consist of bound notebooks with pre-numbered pages, personnel qualification and training forms, equipment maintenance and calibration forms, chain-of-custody forms, sample analysis request forms, and analytical change request forms. All records should be written in indelible ink.

Procedures for reviewing, approving, and revising laboratory records should be clearly defined, with the lines of authority included. As a minimum, all documentation errors should be corrected by drawing a single line through the error so that it remains legible and should be initialed by the responsible individual, along with the date of change. The correction is written adjacent to the error.

Strip-chart recorder printouts should be signed by the person who performed the instrumental analysis. If corrections need to be made in computerized data, a system parallel to the corrections for handwritten data should be in place.

Records of sample management should be available to permit the re-creation of an analytical event for review in the case of an audit or investigation or a dubious result.

Laboratory records should include, at least, the following:

Operating Procedures -- Procedures should be available to those performing the task outlined. Any revisions to laboratory procedures should be written, dated, and distributed to all affected individuals to ensure implementation of changes. Areas covered by operating procedures are given in Section 3.5 and 4.5.

Quality Assurance Plans -- The QAPP/SOPs should be on file.

Equipment Maintenance Documentation -- A history of the maintenance record of each system serves as an indication of the adequacy of maintenance schedules and parts inventory. When maintenance is necessary, it should be documented in either standard forms or in logbooks. Maintenance procedures should be clearly defined and written for each measurement system and required support equipment.

Proficiency -- Proficiency information on all compounds reported should be maintained and should include (1) precision; (2) bias; (3) method detection limits; (4) spike recovery, where applicable; (5) surrogate recovery, where applicable; (6) checks on reagent purity, where applicable; and (7) checks on glassware cleanliness, where applicable.

Calibration Records & Traceability of Standards/Reagents -- Calibration is a reproducible reference point to which all sample measurements can be correlated. A Sound calibration program should include provisions for documenting frequency, conditions, standards, and records reflecting the calibration history of a measurement system. The accuracy of the calibration standards is important because all data will be in reference to the standards used. A program for verifying and documenting the accuracy and traceability of all working standards against appropriate primary grade standards or the highest quality standards available should be routinely followed.

Sample Management -- All required records pertaining to sample management should be maintained and updated regularly. These include chain-of-custody forms, sample receipt forms, and sample disposition records.

Original Data -- The raw data and calculated results for all samples should be maintained in laboratory notebooks, logs, bench sheets, files or other sample tracking or data entry forms. Instrumental output should be stored in a computer file or a hard-copy report.

QC Data -- The raw data and calculated results for all QC and field samples and standards should be maintained in the manner described in the preceding paragraph. QC samples include, but are not limited to, control samples, method blanks, matrix spikes, and matrix spike duplicates.

Correspondence -- Project correspondence can provide evidence supporting technical interpretations. Correspondence pertinent to the project should be retained and placed in the project files.

Deviations -- All deviations from procedural and planning documents should be recorded in laboratory notebooks. Deviations from QAPPs are to be reviewed and approved by the authorized personnel who performed the original technical review or by their designers.

Final Report -- A copy of any report issued and any supporting documentation should be retained.

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Part V.

Laboratory Quality Program and Analytical Guidelines

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PART V.

Laboratory Quality Program and Analytical Guidelines

1.0 INTRODUCTION[αΩ]

This chapter provides guidance for obtaining and documenting analytical data of appropriate quality to meet project objectives. The guidance in this chapter is based on the analytical methods as specified in *Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods***,** U.S. EPA Publication SW-846**,** Third Edition, and promulgated updates. A working knowledge of SW-846 and the basic understanding of analytical process are necessary to understand this chapter. The principles set forth in this chapter are adaptable to aid in the quality control and quality assurance of other applicable methods. Since it is not practical to prepare ~~a~~ guidance for every analytical method or technique, this document focuses on those most commonly used in the environmental field. The analytical techniques discussed in this chapter are:

- Atomic Absorption Spectroscopy (flame and furnace AA),
- Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP),
- Inductively Coupled Plasma Atomic Emission Spectroscopy/Mass Spectrometry (ICP/MS) (limited discussion)
- Gas Chromatography**/**Mass Spectrometry (GC/MS),
- Gas Chromatography with Electron Capture Detector (GC/ECD),
- High Performance Liquid Chromatography (reverse phase HPLC), and
- limited wet chemistry techniques.

Analytical results and data quality interpretation, inferences**,** or extrapolations are dependent on variations in samples, aliquots, matrices, instruments, analysts, methods, etc. In many if not most cases, the analyst will be required to use professional judgement. Therefore, the tables provided are to be used with caution to determine if data quality has been affected or if corrective action steps are necessary. Control limits, spiking concentrations, calibration ranges, and many other criteria may need to be modified to accommodate the characteristics of a particular sample set or to meet project-specific data quality objectives.

1.1 Purpose of a Laboratory Quality System

The purpose of a laboratory quality control system and the documentation of that system through quality assurance practices is to verify the analytical performance. The scientific defensibility of data is predicated on the performance of the analysis. Each quality control item is selected to monitor a specific process or operation within the overall analysis. Through these steps, the accuracy, precision, and bias of data and, therefore, the usability of the data for the specific project objectives, can be determined.

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

Table 1 - METALS[17]				
Holding Times, Digestion Volumes, Collection Volumes and Preservatives for Metals Samples				
Measurement	**Digestion Volume (mL)[a,c]**	**Collection Volume (mL)[a,c]**	**Treatment/ Preservative**	**Holding Time**
Metal Analytes (except hexavalent chromium and mercury)				
Aqueous				
Total Metals	100	600	HNO_3 to pH < 2	6 months
Dissolved Metals	100	600	Filter on site; HNO_3 to pH < 2	6 months
Suspended Metals	100	600	Filter on site	6 months
Soils, Sediments, Sludges, Wastes				
Total Metals	2 g	200 g	-----	6 months
Hexavalent Chromium (Cr^{6+})				
Aqueous				
All Aqueous	100	400	Store at 4 ± 2 C until analyzed	24 hours
Soils, Sediments, Sludges, Wastes				
All Solids	2.5 g	100 g	Store at 4 ± 2 C until analyzed	1 month to extraction; 4 days after extraction
Mercury				
Aqueous				
Total Hg	100	400	HNO_3 to pH < 2	28 days
Dissolved Hg	100	400	Filter; HNO_3 to pH < 2	28 days
Soils, Sediments, Sludges, Wastes				
Total Hg	0.2 g	200 g	Store at 4 ± 2 C until analyzed	28 days

[17]Adapted from *SW-846*, Third Edition, *Final Update III* (December 1996), Chapter Three, Table 3-1, Rev. 3, THREE-4.

Table 1 - ORGANICS[18]			
Sample Containers, Preservation, Techniques, and Holding Times for Organic Samples			
VOLATILE ORGANICS			
Sample Matrix	**Container**	**Preservative & Treatment**	**Holding Time**
Concentrated Waste Samples	Method 5035: 40-mL vials with stirring bar Method 5021: See method. Methods 5031 & 5032: 125-mL wide mouth glass container. *Use Teflon-lined lids for all procedures.*	Cool to 4 C.	14 days
Aqueous samples: *NO residual chlorine present*	Methods 5030, 5031, & 5032: 2 x 40-mL vials with Teflon-line septum caps.	Cool to 4 C *and* adjust pH to < 2 with H_2SO_4, HCL, or solid $NaHSO_4$.	14 days
Aqueous samples: *WITH residual chlorine present*	Methods 5030, 5031, & 5032: 2 x 40-mL vials with Teflon-line septum caps.	*Collect sample in a 125-mL container which has been pre-preserved with 4 drops of 10% sodium thiosulfate solution*. Gently swirl to mix sample, then: transfer to a 40-mL VOA vial. Cool to 4 C and adjust pH to < 2 with H_2SO_4, HCL, or solid $NaHSO_4$.	14 days
Acrolein and Acrylonitrile *in aqueous samples*	Methods 5030, 5031, & 5032: 2 x 40-mL vials with Teflon-line septum caps.	Adjust to pH 405. Cool to 4 C.	14 days
Solid Samples (Soils, Ash, Sediments, Sludges, etc.)	Method 5035: 40 mL-vials with septum and Stirring bar. Method 5021: See method. Methods 5031 & 5032: 125-mL wide mouth Glass container with Teflon-lined lids.	See the individual methods.	14 days

[18]Adapted from *SW-846*, Third Edition, *Final Update III* (December 1996), Chapter Four (Rev. 3), Table 4-1, FOUR-6.

Table 1 - ORGANICS[19], continued			
Suggested Sample Containers, Preservation, Techniques, and Holding Times for Organic Samples			
SEMIVOLATILE ORGANICS			
Sample Matrix	**Container**	**Preservative & Treatment**	**Holding Time**
Concentrated Waste Samples	125-mL wide mouth glass with Teflon-lined lid	None	*Extract sample* within **14** days; *Analyze extract* within **40** days
Aqueous samples: *NO residual chlorine present*	1-gallon, 2 x 0.5-gallon, or 4 x 1-L amber glass container with Teflon-lined lids	Cool to 4 C.	*Extract sample* within **7** days; *Analyze extract* within **40** days
Aqueous samples: *WITH residual chlorine present*	1-gallon, 2 x 0.5-gallon, or 4 x 1-L amber glass container with Teflon-lined lids	3-mL 10% sodium thiosulfate solution per gallon (or 0.008%). Cool to 4 C.	*Extract sample* within **7** days; *Analyze extract* within **40** days
Solid Samples (Soils, Ash, Sediments, Sludges, etc.)	250-mL wide mouth glass container with Teflon-lined lid.	Cool to 4 C.	*Extract sample* within **14** days; *Analyze extract* within **40** days

[19]Adapted from *SW-846*, Third Edition, *Final Update III* (December 1996), Chapter Four (Rev.3), Table 4-1, FOUR-7.

Table 1 Supplemental: **CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES FOR AQUEOUS SAMPLES**[20]

Analysis Name	Container*	Preservation	Max. Holding Time
Bacteriological Tests:			
Coliform, fecal and total	P,G	Cool, 4 C, 0.008%, $Na_2S_2O_3$	6 hours
Fecal streptococci	P,G	Cool, 4 C, 0.008%, $Na_2S_2O_3$	6 hours
Metals:			
Chromium VI	P,G	Cool, 4 C	24 hours
Mercury	P,G	HNO_3 to pH < 2	28 days
Metals (except chromium VI and mercury)	P,G	HNO_3 to pH < 2	6 months
Inorganic Tests:			
Acidity	P,G	Cool, 4 C	14 days
Alkalinity	P,G	Cool, 4 C	14 days
Ammonia	P,G	Cool, 4 C, H_2SO_4 to pH < 2	28 days
Biochemical oxygen demand	P,G	Cool, 4 C	48 hours
Bromide	P,G	None required	28 days
Biochemical oxygen demand Carbonaceous	P,G	Cool, 4 C	48 hours
Chemical oxygen demand	P,G	Cool, 4 C, H_2SO_4 to pH < 2	28 days
Chloride	P,G	None required	28 days
Chloride, total residual	P,G	None required	Analyze immediately
Color	P,G	Cool, 4 C	48 hours
Cyanide, total and amenable to chlorination	P,G	Cool, 4 C, NaOH to pH > 12 0.6g ascorbic acid	14 days
Fluoride	P	None required	28 days
Hardness	P,G	HNO_3 to pH < 2, H_2SO_4 to pH < 2	6 months
Hydrogen ion (pH)	P,G	None required	Analyze immediately
Kjeldahl and organic	P,G	Cool, 4 C, H_2SO_4 to pH < 2	28 days
Nitrate	P,G	Cool, 4 C	48 hours
Nitrate-nitrite	P,G	Cool, 4 C, H_2SO_4 to pH < 2	28 days
Nitrite	P,G	Cool, 4 C	48 hours
Oil and grease	G	Cool, 4 C, H_2SO_4 to pH < 2	28 days
Organic carbon	P,G	Cool, 4 C, HCl or H_2SO_4 to pH < 2	28 days
Orthophosphate	P,G	Filter immediately, cool, 4 C	48 hours
Oxygen, Dissolved Probe	G (bottle & top)	None required	Analyze immediately
Winkler	do	Fix on site and store in dark	8 hours
Phenols	G only	Cool, 4 C, H_2SO_4 to pH < 2	28 days
Phosphorus (elemental)	G	Cool, 4 C	48 hours
Phosphorus, total	P,G	Cool, 4 C, H_2SO_4 to pH < 2	28 days
Residue, total	P,G	Cool, 4 C	7 days
Residue, Filterable	P,G	Cool, 4 C	7 days
Residue, Nonfilterable (TSS)	P,G	Cool, 4 C	7 days
Residue, Settleable	P,G	Cool, 4 C	48 hours
Residue, Volatile	P,G	Cool, 4 C	7 days

[20]Adapted from *SW-846*, Third Edition, (September 1996), Chapter Two, Table 2-16, Rev. 0, TWO-31,32.

*****Polyethylene (P) or Glass (G)

Supplemental Table 1: **CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES FOR AQUEOUS SAMPLES**

Analysis Name	Container*	Preservation	Max. Holding Time
Silica	P	Cool, 4 C	28 days
Specific conductance	P,G	Cool, 4 C	28 days
Sulfate	P,G	Cool, 4 C	28 days
Sulfide	P,G	Cool, 4 C, add zinc acetate Plus sodium hydroxide pH > 9	7 days
Sulfite	P,G	None required	Analyze immediately
Surfactants	P,G	Cool, 4 C	48 hours
Temperature	P,G	None required	Analyze
Total organic carbon (TOC)	P,G	Cool, 4 C, HCl or H_2SO_4 to pH < 2	28 days
Turbidity	P,G	Cool, 4 C	48 hours
Organic Tests:			
Purgeable halocarbons	G, Teflon-lined septum	Cool, 4 C, 0.008%, $Na_2S_2O_3$	14 days
Purgeable aromatic hydrocarbons	G, Teflon-lined septum	Cool, 4 C, 0.008%, $Na_2S_2O_3$, HCl to pH2	14 days
Acrolein and acrylonitrile	G, Teflon-lined septum	Cool, 4 C, 0.008%, $Na_2S_2O_3$, Adjust pH to 4-5	14 days
Phenols	G, Teflon-lined cap	Cool, 4 C, 0.008%, $Na_2S_2O_3$	7 days until extraction 40 days after extraction
Benzidines	G, Teflon-lined cap	Cool, 4 C, 0.008%, $Na_2S_2O_3$	7 days until extraction
Phthalate esters	G, Teflon-lined cap	Cool, 4 C	7 days until extraction 40 days after extraction
Nitrosamines	G, Teflon-lined cap	Cool, 4 C, store in dark, 0.008%, $Na_2S_2O_3$	40 days after extraction
PCBs, acrylonitrile	G, Teflon-lined cap	Cool, 4 C	40 days after extraction
Nitroaromatics and isophorone	G, Teflon-lined cap	Cool, 4 C, 0.008%, $Na_2S_2O_3$ store in dark	40 days after extraction
Polynuclear aromatic hydrocarbons	G, Teflon-lined cap	Cool, 4 C, 0.008%, $Na_2S_2O_3$ store in dark	40 days after extraction
Haloethers	G, Teflon-lined cap	Cool, 4 C, 0.008%, $Na_2S_2O_3$ store in dark	40 days after extraction
Chlorinated hydrocarbons	G, Teflon-lined cap	Cool, 4 C	40 days after extraction
TCDD	G, Teflon-lined cap	Cool, 4 C, 0.008%, $Na_2S_2O_3$	40 days after extraction
Total organic halogens (TOX)	G, Teflon-lined cap	Cool, 4 C, H_2SO_4 to pH < 2	7 days
Pesticides Tests:			
Pesticides	G, Teflon-lined cap	Cool, 4 C, pH 5-9	40 days after extraction
Radiological Tests:			
Alpha, beta and radium	P,G	HNO_3 to pH < 2	6 months

***Polyethylene (P) or Glass (G)

1.2 Personnel

The facility or their representative must designate and utilize key personnel qualified to perform laboratory analysis to the QA/QC levels specified in the facility's Quality Assurance Project Plan.

The laboratory should have a training program in place. Individual training records should be kept for all personnel, documenting areas of training and skill levels achieved. Laboratory staff should demonstrate proficiency in the technique and execution of a given analytical method and in the operation of the associated equipment or instrumentation before unsupervised performance.

2.0 INORGANIC AND GENERAL ANALYSIS

This section provides guidance for QA/QC measures for determinative analyses of metal analytes, general inorganic analytes, and wet chemistry techniques. This section also applies to non-specific organic analyses, such as total organic carbon (TOC) and total organic halides (TOX), for which the analytical procedures and QA/QC measures are similar to those for general inorganic analyses.

This section summarizes requirements for metals analysis by ICP, ICP/MS, flame AA, and graphite furnace AA. It also addresses requirements for general inorganic analyses and wet chemistry performed by techniques such as spectrophotometry, colorimetry, and potentiometric determinations.

2.1 Method Selection

Atomic absorption spectroscopy (flame, graphite furnace, and cold vapor); inductively coupled plasma atomic emission spectroscopy, and general inorganic methods can be used to produce data of appropriate quality for the analysis of environmental and waste samples. However, data quality can be greatly enhanced when the analyst understands both the intended use of the results and the limitations of the specific analytical procedures available to produce the data. The combination of preparatory and determinative methods selected for analysis should be those most suitable to meet the DQO requirements, taking sample characteristics into account.

Sample preparation methods and determinative analytical methods should be selected based upon the analyte (or analytes) to be measured, sample matrix characteristics (phase and potential interferences), and the data quality objectives of the project. Special note should be made of detection limit requirements based on regulatory limits or risk-based health protective levels to which concentrations will be compared. Special attention should also be paid to sample characteristics requiring alternate handling, preparation, or analysis techniques.

2.1.1 Sample Characteristics and Project Objectives

In order to choose the correct combination of methods (preparatory and determinative) to comprise the appropriate analytical procedure, the following basic information must be known:

- Phase characteristics of the sample. This includes whether the sample is aqueous, soil, sludge, oil, liquid waste, sediment, multiphasic, etc.[21] Different handling procedures, preparatory methods and, sometimes, different determinative methods are used for samples of various phase characteristics.

- Analytes of interest. The nature of the target analytes may dictate special handling, preparation, or analytical techniques or very specific short-term analytical holding times.

- Potential interferences. Chemicals (other than the target analytes) known or suspected of being present in the sample that might interfere with analysis or detection, should also be taken into account when selecting a method or determining if sample cleanup is required.

- Detection Limits. Depending on the project objective and intended end use of the data, specific detection limits may be required. It may be intended to compare the target analyte concentrations to risk-based human health or ecological protective levels, drinking or water detection limits, or regulatory limits such as TCLP or Maximum Contaminant Levels (MCLs). If the detection limit exceeds the comparison value, environmental protection or compliance to regulations cannot be determined. Different determinative methods have different levels of sensitivity and should be chosen accordingly. The preparatory or extraction method can also affect the final detection limit.

- Analytical Objective. The intended use of the data should be communicated to the laboratory analyst. The analytical or project objective could affect choice of preparatory and determinative methods. It can also affect the format and detail in which the data is reported, as well as whether concentrations are reported in wet weight or dry weight and in which units of measurement.

2.1.2 Project-Specific Factors

Project specific factors can affect the effectiveness and quality of the data as well as the cost of the analytical process. The greater the available information about the site, unit, waste generation process, or contaminant source, the better the selection of analytical process can be.

If the DQO requires low detection limits for metals is aqueous samples, it may be necessary to select trace ICP or graphite furnace AA analysis rather than standard ICP or flame AA.

Samples to undergo metals analysis by atomic absorption or ICP spectroscopy must first undergo acid digestion. Separate digestion preparation methods exist for aqueous, solids, and oily wastes and for whether total, dissolved, or suspended metals will be measured. *SW-846* Chapter Three includes a variety of extraction and solubilization methods to

[21]The phase of the sample is often incorrectly referred to as the sample "matrix." The matrix, in actuality, includes all characteristics and components of the sample. I.e., the matrix includes the substrate containing the analytes of interest (i.e., the material the phase characteristics describe, the analytes of interest (or target analytes), and all other chemicals found in the substrate: naturally occurring species, anthropogenic materials, and contaminants that are not target analytes.

accommodate various sample characteristics and analytical objectives. It should be noted that, since chlorine is an interferent in ICP/MS analysis, the use of hydrochloric acid is not recommended for digestion of samples to be analyzed by ICP/MS. To prepare samples for general inorganic analysis, refer to the individual method.

ICP/MS analysis requires additional QA/QC measures beyond those required for other inorganic analyses. Refer to Section 2.15, below, for a discussion of specialized ICP/MS requirements.

2.2 Inorganic Analysis Quality Assurance/Quality Control Measures

The quality control measures generally performed for metals, general inorganic, and general wet chemistry analysis are summarized below, along with the reasons they are necessary. A more detailed outline with recommended control limits is provided in section 2.3. Documentation and deliverables requirements are listed in Appendix II.

Chain-of-Custody: A chain-of-custody procedure should be followed and documented to ensure the traceability through shipment and identity, security, and physical integrity of samples upon receipt at the laboratory. A chain-of-custody form should be initiated by the individual(s) taking the sample and surrendered to laboratory staff with the field samples. The laboratory may also choose to use an internal chain-of-custody process.

All samples should be stored in a separate storage area accessible to authorized personnel only. Access to samples must be restricted to authorized personnel at all times. Sample chain-of-custody within the laboratory should be consistent with the security procedures used by EPA-NEIC (National Enforcement Investigations Center) facilities.

Instrument Detection Limit Determination: An IDL determination should be performed on each instrument for each analyte measured prior to any sample analysis on that instrument. The determination should be repeated at least annually and after any significant instrument modifications.

Method Detection Limit Studies: Method Detection Limit Studies must be performed and documented for each analytical method run by the laboratory. A separate detection limit study must be performed for each sample matrix type analyzed and for each instrument used to run a particular method. The detection limit studies should be performed annually and whenever an instrument modification occurs, a new instrument is added, or a new sample matrix type is analyzed.

Holding Time Specifications: It is the facility's or their representative's responsibility to ensure that the analyses are performed within the specified time limits. The required time limits for metals analyses of various matrix types are given in Table 1-Metals. Required time limits for metals, general inorganics, and wet chemistry analyses of aqueous samples are given in Supplemental Table 1. The holding time clock begins at the moment the sample is taken.

Calibration: The instrument or analytical equipment is calibrated in order to establish an accuracy range within which a known response results from a specific concentration of analyte. Calibration delineates the relationship between the concentration of analyte introduced into the instrument and the instrument response.

Continuing Calibration or Initial and Continuing Calibration Verification: The continuing calibration sample is analyzed at a specific frequency throughout the analytical run in order to confirm that the instrument or analytical equipment has remained in calibration.

Instrument Blank: The instrument blank, sometimes referred to as the calibration blank, has a twofold purpose. Initially it is used to assess the instrument or equipment's performance (e.g., instrument noise) without the analyte being present. Secondly, it is used to confirm that there was no carryover between analyses or that response has not changed throughout the analysis. The instrument blank is analyzed at the beginning of analysis and at a specific frequency throughout the analytical run. The instrument blank analyzed at the beginning of the run is sometimes called the initial calibration blank (ICB); those analyzed throughout the run are sometimes called the continuing calibration blank(s) (CCB).

Method Blank: The method blank, sometimes referred to as the preparation blank, is used to verify that contamination was not introduced into the analyses by sample handling, including the preparation step and sample analysis. The method blank is handled and analyzed in the same manner as the samples. The method blanks are analyzed at a specific frequency throughout the analytical run. At a minimum, this frequency should be 1 blank per each group of up to 20 samples prepared at the same, by the same procedures, and analyzed on the same instrument during the same analytical shift.

Matrix Spike: An actual sample is spiked before the preparation step with the analyte of interest at a known concentration in order to determine if the sample matrix is interfering with the analyte response. The matrix spike is used to assess the accuracy of the analysis in the actual sample matrix. The matrix spike samples are analyzed at a specific frequency throughout the analytical run.

Matrix Spike Duplicate: A second matrix spike is prepared and analyzed as before in order to confirm that there is consistency in preparation and analysis. The matrix spike duplicate is used to assess analytical precision. The matrix spike duplicates are analyzed at a specific frequency throughout the analytical run.

Duplicate Sample Analysis: A laboratory duplicate sample, also referred to as a matrix duplicate, is prepared and analyzed in order to confirm that there is consistency in preparation and analysis. Analysis of laboratory duplicate samples is used to assess analytical precision. Laboratory duplicate samples are analyzed at a specific frequency throughout the analytical run. Some methods specify analysis of a matrix duplicate in place of a matrix spike duplicate .

Field Duplicate Analysis: A field duplicate sample is collected at a specified frequency during field activities. The field duplicates are treated as independent samples during laboratory processes of preparation and analysis. Analysis of field duplicate samples is used to assess variability introduced by the sampling process and sample matrix homogeneity.

Laboratory Control Sample: A blank is spiked with the analyte of interest before the preparation step and analyzed in the same manner as the samples to verify that the analytical method is within control. The results of the laboratory control samples are used to assess if poor analytical performance is matrix dependent or an analytical method problem (in conjunction with the matrix spike). The laboratory control sample is analyzed at a specific frequency throughout the analytical run.

Standard Addition: The standard addition technique involves adding known amounts of standards to one or more aliquots of the processed sample solution (i.e., after sample preparation). The analyte concentration is then calculated from the standard addition and compared to the calibration curve. This technique compensates for interferences that can cause enhancement or suppression of the analyte signal.

Serial Dilution: The serial dilution technique is performed in order to verify that there is not an interference problem throughout the linear range of the instrument. This technique is used for inductively coupled plasma (ICP) metal analysis and graphite furnace metal analysis routinely; however, it may also be used with other analysis methods where interferences are suspected.

ICP Interference Check Sample: For ICP analysis, a sample containing known concentrations of compounds that interfere with the signals of the compounds of interest is analyzed to assess the effectiveness of the interelement correction factors.

ICP Interelement Correction Factors: Interelement correction factors are used to correct for spectral interferences caused by aluminum, calcium, iron, and magnesium (and sometimes for other elements) in the samples. Correction factors should be determined for all ICP instruments at all wavelengths used for each analyte reported by ICP. The determination should be repeated at least annually and after any significant instrument adjustment or modification.

ICP Linear Range Determination Analysis: The upper limit of the linear dynamic range must be established for each wavelength utilized by determining the signal responses from a minimum for three, preferably five, different concentration standards across the range. One of these should be near the upper limit of the range. The ranges which may be used for the analysis of samples should be judged by the analyst from the resulting data. For those analytes that periodically approach the upper limit, the range should be checked every six months. Some methods require a quarterly verification of the upper limit using a high concentration check standard.

Specific methods may require additional quality control measures, beyond those listed above, in order to verify that the analysis was under control at each step of the process. In addition, specific sample matrices may require additional quality control analyses to determine whether positive or negative interferences are operating on any of the analytes to distort the accuracy of the reported values and, if so, to determine the direction and magnitude of bias.

Specialized instrumental methods may require a different list of quality control measures than those listed above (e.g., ICP/MS). Follow instructions in the individual analytical method and manufacturer's recommended procedures.

2.3 Reporting

This section outlines the minimum Quality Assurance/Quality Control operations necessary to satisfy the analytical requirements for metals and inorganic analysis. The following QA/QC operations should be performed and reported as stated in this section. In order for data to be considered as analytically valid, all QA/QC must be documented and reported with the analytical results. Deliverables requirements for documentation of QA/QC measures and data are listed in Appendix II.

2.3.1 Instrument Detection Limit Determination

Before any field samples are analyzed, the instrument detection limits (IDL) must be established. The IDLs should meet the specified requirements in the analytical methods. The instrumental detection limits should be determined by following the instrument manufacturer's recommendations and the individual method requirements. (See also SW-846 Chapter Three, Method 6010B, and Method 7000A, and USEPA Contract Laboratory Program (CLP) Statement of Work (SOW) for Inorganics Analysis, ILM04.0 Exhibit E.) For each case, the relevant IDLs must be reported on the QC Report. If multiple instruments are used for the analysis of an element or compound within a case, the IDLs for each instrument must be reported.

2.3.2 Method Detection Limit Determinations for Each Matrix

Method Detection Limit Studies must be performed and documented for each analytical method run by the laboratory. A separate detection limit study must be performed for each sample matrix type analyzed and for each instrument used to run a particular method.

To determine an MDL for a given analyte in a given matrix, the following procedure may be used. (Also see SW-846 Chapter One and Appendix B to 40 CFR Part 136.):

The standard deviation obtained from three or more replicate analyses of a matrix spike containing the analyte of interest (at a concentration three to five times the *estimated* MDL) is multiplied by the appropriate one-sided, 99% confidence level t-statistic by. The t-statistic is obtained from standard references or from the table below.

No. of samples:	t-statistic	No. of samples:	t-statistic
3	6.96	7	3.14
4	4.54	8	3.00
5	3.76	9	2.90
6	3.36	10	2.82

For purposes of choosing the analyte concentration for the replicate analyses, the MDL is estimated as the concentration value that corresponds to either:

a) an instrument signal/noise ratio within the range of 2.5 to 5.0, *or*
b) the region of the standard curve where there is a significant change in sensitivity (i.e., a break in the slope of the standard curve).

Determine the MDL for each analyte as follows:

$$\mathbf{MDL} = \mathbf{t}_{(n-1,a = .99)}(\mathbf{s})$$

where **s** is the standard deviation of the replicate analyses,
and $\mathbf{t}_{(n-1,a = .99)}$ is the one-sided t-statistic appropriate for the number of samples used to determine **s**, at the 99 percent confidence level.

2.3.3 Initial Calibration

Calibration of an analytical instrument involves the delineation of the relationship between the response of the instrument and the amount or concentration of an analyte introduced into the instrument. The graphical depiction of this relationship is often referred to as the calibration curve. In order to perform quantitative measurements, this relationship must be established prior to the analysis of any samples, and thus, is termed initial calibration.

Guidelines for instrumental calibrations are given in and in the individual analytical methods. (Also see SW-846 Method 7000A.) *Instruments must be calibrated daily* or, if the analysis is not run on a daily basis, each time the instrument is set up.

2.3.3.1 FOR ATOMIC ABSORPTION (AA) SYSTEMS, calibration standards are prepared by diluting the stock metal solutions at the time of analysis. For best results, calibration standards should be prepared fresh each time a batch of samples is analyzed. Low calibration standards must be prepared fresh each time an analysis is to be performed and discarded after each use. Prepare a calibration blank and minimum of three calibration standards in graduated amounts in the appropriate range (linear part of the curve). One atomic absorption calibration standard must be at the at the estimated quantitation limit (EQL).

The calibration standards should be prepared using the same type of acid or combination of acids as was used in sample preparation. The concentration of acid(s) in the standards should be at the same concentration as will result in the samples following processing. Beginning with the blank and working toward the highest standard, aspirate or inject the solutions and record the readings. Repeat the operation with both the calibration standards and the samples a sufficient number of times to secure a reliable average reading for each solution. Calibration standards for furnace procedures should be prepared as described on the individual sheets for that metal. Linear calibration curves are always required. *The correlation coefficient of the line of the calibration curve must be equal to or greater than 0.995.*

2.3.3.2 FOR CYANIDE, MERCURY, AND OTHER INORGANICS ANALYSES, follow the calibration procedures outlined in the analytical method. One calibration standard should be at the EQL. Calibration curves must be linear. *The correlation coefficient of the line of the calibration curve must be equal to or greater than 0.995.*

2.3.3.3 FOR ICP SYSTEMS, calibrate the instrument according to instrument manufacturer's recommended procedures.

If an ICP/MS system is used, the mass spectrometer must be tuned to ensure that mass calibration and resolution are within required specifications. This must be done in addition to calibration of the ICP. Also, internal standards must be added to all field samples, quality control samples, and calibration standards. (See SW-846 Method 6020 and instrument manufacturer’s instructions.)

2.3.4 Initial and Continuing Calibration Verification

After instrument calibration has been performed, the accuracy of the initial calibration must be verified and documented for every analyte by the analysis of an initial calibration

verification solution. To ensure calibration accuracy throughout the analytical run, a continuing calibration verification standard must be run at periodic intervals.

2.3.4.1 INITIAL CALIBRATION VERIFICATION (ICV). The accuracy of the initial calibration is verified by the analysis of at least a calibration blank and a calibration check standard, often referred to as an initial calibration verification standard or solution (ICV). The ICV should be made from a reference material or other independent standard material at or near the mid-range. An independent standard is defined as a standard composed of the analytes from a different source than that used in the standards for the initial calibration. The initial calibration verifications must be analyzed at the beginning of analysis.

The initial calibration verification standard must be run under the same conditions used for analysis. For ICP analysis, the initial calibration verification solution must be run at each wavelength used in the analysis of the sample. A certified standard analyte solution should be used. If a certified solution of an analyte is not available from any source, analyses shall be conducted on an independent standard at a concentration other than that used for calibration, but within the calibration range. The measured concentration of the ICV must be within the percentage of its true value indicated in Table 2 for the curve to be considered valid. When measurements exceed the control limits of Table 2, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.

For cyanide analyses in which the analytical method calls for distillation of samples, it is also recommended that at least two standards (a high and a low) be distilled and compared to similar values for undistilled standards on the curve to ensure that the distillation technique is reliable. If distilled standards do not agree within + 10% of the undistilled standards, the analyst should find the cause of the apparent error before proceeding.

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2.3.4.2 CONTINUING CALIBRATION VERIFICATION (CCV). If more than 10 samples per day are analyzed, the working standard curve must be verified by measuring satisfactorily a mid-range standard or reference standard after every 10 samples, or 1 per sample set whenever the sample set is less than 10. Every effort should be made to analyze the facility's samples as a set. If samples other than the facility's samples are prepared for analysis in a set with the facility's samples, these samples are to be regarded as part of the 1 in 10 frequency. One continuing calibration verification standard must also be performed for each analyte at the beginning of the run and after the last analytical sample. The analyte concentrations in the continuing calibration standard should be at or near the mid-range levels of the calibration curve. The standard should be prepared from one of the following solutions:

- EPA Solutions,
- NIST Standards, or
- A laboratory-prepared standard solution.

The same continuing calibration standard must be used throughout the analysis runs for a case (i.e., set or batch) of samples received. A log of spiking solutions, preparation, and sources should be maintained.

If the deviation of the continuing calibration verification is greater than the control limits specified in Table 2, the instrument must be recalibrated and the preceding 10 samples

reanalyzed for the analytes affected. Information regarding the continuing verification of calibration should be recorded and reported.

TABLE 2

Initial and Continuing Calibration Verification Control Limits for Inorganic Analyses[α]

Analytical Method	Inorganic Species	% of True Value (EPA Set)	
		Low Limit	High Limit
ICP/AA (except cold vapor)	Metals	90	110
Cold Vapor AA	Mercury	80	120
Other	Cyanide/Sulfide	85	115
Other	General Inorganic & Wet Chemistry	90	110

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

2.3.5 Calibration Blank Analysis

A calibration (or instrument) blank is analyzed each time the instrument is calibrated, at the beginning and the end of the run, and at a frequency of 10% during the run directly after the continuing calibration standard is analyzed. The results for the calibration blank solution should be recorded and reported. Blanks results are to be reported whether "negative" or "positive". If the absolute value of the blank result is greater than the EQL, terminate analysis, correct the problem, and recalibrate.

2.3.6 Method (Preparation) Blank Analysis

At least one preparation blank (or reagent blank), consisting of deionized distilled water processed through each sample matrix preparation procedure (i.e., one each for water, solids, sludges, oils, etc.) performed for each case, should be prepared and analyzed with every 10 samples received or with each batch (a group of samples prepared at the same time) of samples digested, whichever is more frequent. The first 10 samples of a case are to be assigned to preparation blank one, and the second 10 samples to preparation blank two, etc. Each data package should contain the results of all the preparation blank analyses associated with the samples in that case. The method blank must be taken through the entire procedure step by step, including all of the reagents and solvents in the quantity required by the method.

This blank is to be reported for each case (i.e., set) and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner.

1. If the absolute value of the blank is less than the EQL, no corrective action is required.

2. If the absolute value of the blank is above the EQL, the analysis for all samples affected (i.e., all samples prepared with the blank) should be repeated.

2.3.7 Spiked Sample Analysis (Matrix Spike)

The spiked sample analysis or matrix spike (MS) is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before the digestion and prior to any distillation steps (e.g., cyanide analysis). At least one spiked sample analysis should be performed on each group of samples of a similar matrix type from the same project (e.g., water, sludges, soil) and concentration (e.g., low, medium) for each group of 10 (or fewer) samples received per project. However, it is not necessary to spike samples when the concentration of the analyte in the unspiked sample exceeds 0.1%.

The matrix spike is a measure of the bias attributed to sample matrix effects, not just laboratory process effects on phase or concentration characteristics. The sample matrix includes the target and non-target analytes present in the sample or group of samples: naturally occurring compounds as well as contaminants. Therefore, the spiked sample must be from the same project as the case of field samples. *If the spiked sample is not from the same project as the field samples, matrix effects cannot be determined and sample results must be qualified as estimated*.

Analyte spiking levels should reflect the concentration range expected to be measured in the field samples for that analyte. If no estimate of the concentration in the field samples is available, the analyte should be spiked at a concentration between the detection limit and the middle of the linear dynamic range (i.e., mid-range) of the calibration curve for each element analyzed. If the mid-range approach is used, and after samples are analyzed measured concentrations are substantially higher or lower than mid-range for any analyte (i.e., near the EQL or near the upper limit of the linear dynamic range), an additional sample spiked at the concentration observed in the field samples should be analyzed.

If two analytical methods are used to obtain the reported values for the same element for a case of samples (e.g., ICP, GFAA), spike samples must be analyzed by each method used. **Samples identified as field blanks cannot be used for spiked sample analysis**.

The % Recovery (%R) for each component should be calculated and reported in the QC report. Individual component percent recoveries are calculated as follows:

$$\%\,\text{Recovery} = \frac{(\text{SSR} - \text{SR})}{\text{SA}} \times 100$$

Where: SSR = Spiked Sample Result
SR = Sample Result

SA = Spike Added

When sample concentration is less than the detection limit, use SR = 0 for purposes of calculating % Recovery. If the spike recovery is not within the limits shown in Table 4, or not within the documented historical acceptance limits for the analyte in that matrix, all samples associated with that spiked sample should be reanalyzed.

TABLE 3
Recommended Concentration Levels for Spiked Sample Analysis[α]

Analyte	For Standard ICP and Flame AA		For Trace ICP and Furnace AA		Other Analysis Types	
	Aqueous g/L	Solid mg/kg	Aqueous g/L	Solid mg/kg	Aqueous g/L	Solid mg/kg
Refer to Section 2.3.7.						

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

2.3.8 Matrix Spike Duplicate Sample Analysis

At least one matrix spike duplicate sample (MSD), prepared identically to the spiked sample for each analyte, should be performed on each group of samples of a similar matrix type from the same project (e.g., water, sludges, soil) and concentration (e.g., low, medium) for each group of 10 (or fewer) samples received per project. However, it is not necessary to spike samples when the concentration of the analyte in the unspiked sample exceeds 0.1%.

Along with the matrix spike, the matrix spike duplicate is a measure of the bias and variability attributed to sample matrix effects, not just laboratory process effects on phase or concentration characteristics. The sample matrix includes the target and non-target analytes present in the sample or group of samples: naturally occurring compounds as well as contaminants. Therefore, the spiked sample and spiked duplicate must be from the same project as the case of field samples. *If the spiked sample and spiked duplicate are not from the same project as the field samples, matrix effects cannot be determined and sample results must be qualified as estimated*. If two analytical methods are used to obtain the reported values for the same element for a case of samples (e.g., ICP, GFAA), duplicate samples should be run by each method used. **Samples identified as field blanks cannot be used for matrix spike duplicate sample analysis**.

The MSD % Recoveries and the relative percent differences (RPD) between the MS and MSD for each analyte should be calculated and reported in the QC report. The relative percent differences for each component are calculated as follows:

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \; x\, 100$$

Where: D_1 = Value for First Duplicate (MS % Rec.)
D_2 = Value for Second Duplicate. (MSD % Rec.)

If the matrix spike duplicate % Recovery or RPD are outside the control limits shown in Table 4 or outside the documented historical acceptance limits for the analyte in that matrix, the analysis should be repeated for all samples associated with that matrix spike duplicate. When the RPD is large, redigestion is also indicated.

TABLE 4

Matrix Spike/Matrix Spike Duplicate Control Limits for Inorganic Analyses[α]

Inorganic Species	% of True *(Spiked)* Value *(%R)*		Relative Percent Difference (RPD)
	Low Limit	High Limit	
Metals	75*	125*	20
Mercury	75	125	20
Cyanide/Sulfide	75	125	20
General Inorganics	75*	125*	20

*In aqueous matrices %R control limits should be set at 80% - 120%.

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

2.3.9 Duplicate Sample Analysis

When a laboratory or matrix duplicate sample is required, one duplicate sample should be analyzed for each matrix type (e.g., water, sludges, soil) and concentration (e.g., low, medium) for each case of samples, or for each 10 samples received, whichever is more frequent. The results should not be averaged; results of each replicate should be reported. **Samples identified as field blanks cannot be used for duplicate sample analysis.**

The RPD for each analyte detected should be calculated and reported in the QC report. The RPD is calculated in the same way for matrix duplicates and laboratory replicates as is

indicated above for matrix spike duplicates. If the RPD exceeds the control limits listed in *TABLE 5*, data should be qualified as estimated.

TABLE 5
Control Limits for Laboratory Duplicate Sample Analysis RPD

Concentration of Analyte in Sample & Laboratory Duplicate	Aqueous Samples	Soil, Sludge, Sediment, Oil, & Waste Samples
Both results Less than (<) 5 X EQL	± EQL value	± 2 X EQL value
Both results Greater than (>) 5 X EQL	± 20 %	± 35%
One result < EQL, one result > EQL	± EQL value	± 2 X EQL value

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

2.3.10 Field Duplicate Sample Analysis

At least one field duplicate sample should be collected for every matrix sampled per sampling event. If large numbers of samples are collected, it is recommended that at least one field duplicate pair be collected for every 20 samples collected. Field duplicates should be treated as independent samples for preparation, analysis, and reporting purposes.

The RPD for each analyte detected should be calculated and reported in the QC report. The RPD is calculated in the same way for matrix duplicates and laboratory replicates as is indicated above for matrix spike duplicates. If the RPD exceeds the control limits listed in *TABLE 5*, data should be qualified as estimated.

TABLE 6
Control Limits for Field Duplicate Sample Analysis RPD

Concentration of Analyte in Sample & Field Duplicate	Aqueous Samples	Soil, Sludge, Sediment, Oil, & Waste Samples
Both results Less than (<) 5 X EQL	± 1.5 X EQL value	± 2.5 X EQL value
Both results Greater than (>) 5 X EQL	± 25 %	± 40 %
One result < EQL, one result > EQL	± 1.5 X EQL value	± 2.5 X EQL value

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

2.3.11 Laboratory Control Sample Analysis (LCS)

Aqueous and solid laboratory quality control samples should be analyzed for each analyte using the same sample preparation and analytical methods employed for the samples received. The aqueous LCS solution should be obtained from EPA (if unavailable, the EPA Initial Calibration Verification solution may be used). One aqueous LCS should be analyzed for every 10 samples received, or for each batch* of samples digested, whichever is more frequent. Each data package should contain the results of all the LCS analyses associated with the samples in that case. For cyanide analysis, the distilled mid-range calibration standard may be used as the aqueous LCS. An aqueous LCS is not required for mercury analysis. All aqueous LCS results will be reported in terms of true concentrations with percent recovery as calculated by:

$$\%R = (\text{Observed}/\text{True}) \times 100$$

Where "observed" is the measured concentration. If the % recovery for the aqueous LCS falls outside the control limits of *TABLE 7*, the analyses should be terminated, the problems corrected, and the previous samples associated with that LCS reanalyzed (i.e., previous 10 samples or the batch of samples from the case).

TABLE 7

Laboratory Control Sample (LCS) Control Limits for Inorganic Analyses[α]

Inorganic Species	% of True *(Spiked)* Value *(%R)*	
	Low Limit	High Limit
Metals	80	120
Mercury	80	120
Cyanide/Sulfide	80	120
General Inorganics	80	120

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

2.3.12 Serial Dilution Analysis for Metals Analysis[22]

Prior to reporting concentration data for the analyte of interest, the laboratory should analyze and report the results of the Serial Dilution Analysis. The Serial Dilution Analysis should be

[22]Note: Serial Dilution Analysis is only *required* for analyses by ICP and GFAA. However, it is *strongly recommended* for metals analyses of all types (e.g., flame AA, cold vapor AA, spectrophotometry). If a three-point MSA will be performed on all samples in the case for a particular analyte(s), Serial Dilution Analysis of the analyte(s) run by MSA is not required for metals analysis by any technique (including ICP and GFAA.)

performed on each group of samples of a similar matrix type (e.g., water, soil) and each concentration (e.g., low, medium) for each case of samples, or for each 10 samples received, whichever is more frequent. **Samples identified as field blanks cannot be used for serial dilution analysis**.

If the analyte concentration is sufficiently high (at least 25 times the estimated detection limit), an analysis of a five-fold (1 + 4) dilution should be performed. The diluted result should agree with the undiluted result within a % Difference (% D) of 10 after correction for dilution. Agreement within 10% between the concentration of the undiluted sample and five times the concentration of the diluted sample indicates the absence of chemical or physical interferences.

The % Difference is calculated as:

$$\%D = \frac{|I - S|}{I} \; x \; 100$$

Where: I = Initial Sample Result
S = Serial Dilution Result (Instrument Reading x 5)

TABLE 8
Serial Dilution Control Limits for Inorganic Analyses[α]

Inorganic Species	% Difference, Dilution vs. Original Determination	
	Low Limit	High Limit
Metals	90	110
Mercury	90	110
Hexavalent Chromium	90	110

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

If the % Difference for serial dilution analysis and the original sample does not meet the control limits of Table 8, a spike recovery test (post-digestion spike) should be performed to confirm the interference problem. If the spike recovery does not meet the control limits of Table 9, all samples in the batch should be analyzed by the method of standard additions.

If all the samples in the batch have analyte concentrations less than 10 times the estimated detection limits, serial dilution analysis should not be performed. Instead, the spike recovery test (analytical spike) should be run. If the spike recovery does not meet the control limits of Table 9, all samples in the batch should be analyzed by the method of standard additions.

Serial dilution and recovery test results should be reported in the QC report.

TABLE 9
Spike Recovery Test Control Limits for Inorganic Analyses[α] to Check for Matrix Interferences

Inorganic Species	% Recovery of Post-Digestion Spike	
	Low Limit	High Limit
Metals	85	115
Mercury	85	115
Cyanide/Sulfide	85	115
General Inorganics	85	115

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

2.3.13 Method of Standard Additions (MSA)

When the matrix interference is indicated, analysis should be performed by the method of standard additions. This technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift.

The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample solution, each of volume V_x , are taken. To the first (labeled A) is added a known volume V_s of a standard analyte solution of concentration C . To the second aliquot (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for non-analyte signals. The unknown sample concentration C_x is calculated:

$$C_x = \frac{S_B V_S C_s}{(S_A - S_B) V_x}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_S and C_S should be chosen so that S_A is roughly twice S_B on the average, avoiding excess dilution of the sample. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

Improved results can be obtained by employing a series of standard additions. To equal volumes of the sample are added a series of standard solutions containing different known quantities of the analyte, and all solutions are diluted to the same final volume. For example, addition 1 should be prepared so that the resulting concentration is approximately 50 percent of the expected absorbance from the endogenous analyte in the sample. Additions 2 and 3 should be prepared so that the concentrations are approximately 100 and 150 percent of the expected endogenous sample absorbance. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated to zero absorbance, the point of interception of the abscissa is the endogenous concentration of the analyte in the sample. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. A linear regression program may be used to obtain this intercept concentration.

2.3.14 ICP Interference Check Sample Analysis (ICS)

To verify interelement and background correction factors, the laboratory should analyze and report the results for an ICP Interference Check Sample at the beginning and end of each sample analysis run, but not before the initial calibration verification. The interference check solution should be prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. The ICS for standard ICP should be spiked with the elements of interest, particularly those with known interferences, at 0.5 to 1 mg/L. ICP/MS analysis will require analysis and checking of a greater number of interferents. For ICP/MS, it is recommended that the elements of interest be spiked at 0.02 mg/L. Chlorine is a an interferent in ICP/MS analysis. The use of chlorine-containing compounds in reagents for sample preparation and analysis should be avoided.

In the absence of measurable analyte, over-correction could go undetected because a negative value could be reported as zero. Therefore, spiked concentrations should be high enough to ensure measurability. If the particular instrument will display over-correction as a negative number, this spiking procedure will not be necessary. Suggested components and concentrations for preparation of the ICS are provided in Table 9-Standard for standard ICP systems and in Table 9-ICP/MS for ICP/MS systems. Other analytes of interest or interferents should be added as necessary to meet project-specific requirements or sample-specific characteristics.

Results for the check sample analysis must fall within the control limits indicated in Table 10 (± 20 % of the true value) for the analytes included in the Interference Check Sample.

Results of all Interference Check Sample analyses for all ICP parameters should be recorded and reported in the QC report.

TABLE 9 - Standard
Suggested Interferent and Analyte Elemental Concentrations αΩ
for Preparation of *Standard ICP* Interference Check Sample

Analyte	**Conc.,** mg/L	**Interferent**	**Conc.,** mg/L
Barium	0.5	Aluminum	500
Beryllium	0.5	Calcium	500
Cadmium	1.0	Iron	200
Cobalt	0.5	Magnesium	500
Chromium	0.5		
Copper	0.5		
Manganese	0.5		
Nickel	1.0		
Lead	1.0		
Vanadium	0.5		
Zinc	1.0		

TABLE 9 - ICP/MS
Suggested Interferent and Analyte Elemental Concentrations αΩ
for Preparation of *ICP/MS* Interference Check Sample

Analyte	**Conc.,** mg/L	**Interferent**	**Conc.,** mg/L
Arsenic	0.0200	Aluminum	100.0
Cadmium	0.0200	Calcium	100.0
Chromium	0.0200	Iron	100.0
Cobalt	0.0200	Magnesium	100.0
Copper	0.0200	Sodium	100.0
Manganese	0.0200	Phosphorus	100.0
Nickel	0.0200	Potassium	100.0
Silver	0.0200	Sulfur	100.0
Zinc	0.0200	Carbon	200.0
		Chlorine	1000.0
		Molybdenum	2.0
		Titanium	2.0

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

TABLE 10

Interference Check Sample Control Limits for Inorganic Analyses[α]

Inorganic Species	% Recovery of Analyte True Value	
	Low Limit	High Limit
Metals	80	120

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

2.3.14 ICP Linear Range Analysis

2.3.14.1 LOW LEVEL CHECK STANDARD**:** To verify linearity near the EQL for ICP analysis, the facility analyze and report an ICP standard at two times the EQL at the beginning and end of each sample analysis run, or at a minimum of twice per hour working shift, whichever is more frequent. This standard should be run for all elements analyzed by ICP, recorded, and reported in the QC report. No specific control criteria have been established for the low level check standard. The analyst and end-user of the data should use professional judgement to qualify data as needed, based on the information provided by the low level check standard results.

TABLE 11

ICP Linear Range Low Level Check Standard Control Limits for Inorganic Analyses[α]

Inorganic Species	% Recovery of Analyte True Value
Metals	No specific control criteria established.

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

2.3.14.2 HIGH LEVEL CHECK STANDARD**:** To verify linearity near the upper end of the linear dynamic range, a quarterly linear range verification check standard must be analyzed and reported for each element. The concentration of the upper level check standard should be selected based on upper limit establishment procedure described in section 2.3.14.3. The standard should be analyzed during a routine analytical run. The analytically determined concentration of this standard should be within ± 5 % of the true value. This concentration is the upper limit of the ICP linear range beyond which results cannot be reported.

TABLE 12

ICP Linear Range High Level Check Standard Control Limits for Inorganic Analyses[α]

Inorganic Species	% Recovery of Analyte True Value	
	Low Limit	High Limit
Metals	95	105

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

2.3.14.3 ESTABLISHMENT OF UPPER LIMIT OF LINEAR RANGE**.** The upper limit of the linear dynamic range must be established for each wavelength utilized by determining the signal responses from a minimum for three, preferably five, different concentration standards across the range. One of these should be near the upper limit of the range. The ranges which may be used for the analysis of samples should be judged by the analyst from the resulting data. The data, calculations and rationale for the choice of range made should be documented and kept on file. The upper range limit should be an observed signal no more than 10% below the level extrapolated from lower standards. New dynamic ranges should be determined whenever there is a significant change in instrument response.

2.3.15 Additional QA/QC Requirements for ICP/MS Analysis

ICP/MS analysis requires the following additional QA/QC measures:

2.3.15.1 INSTRUMENT TUNING**.** Prior to calibration and analysis, the mass spectrometer must be tuned. A solution containing elements representing all of the mass regions of interest (for example, 10 µg/L each of Li, Co, In, and Tl) must be prepared to verify that the resolution and mass calibration of the instrument are within the required specifications. This solution is also used to verify that the instrument has reached thermal stability.

2.3.15.1(a) Verification of Thermal Stability. The analyst should follow the instructions provided by the instrument manufacturer. Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples. This must be verified by analyzing a tuning solution at least four times with relative standard deviations of < 5% for the analytes contained in the tuning solution.

NOTE: Precautions must be taken to protect the channel electron multiplier from high ion currents. The channel electron multiplier suffers from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. *During this time period, response factors are constantly changing, which invalidates the calibration curve, causes instability, and invalidates sample analyses.*

TABLE 13

ICP/MS Tuning Control Limits to Verify Thermal Stability for Inorganic Analyses[α]

Inorganic Species	Relative Standard Deviation (RSD) for Four Analyses of Analytes in Tuning Solution	
	Low Limit	High Limit
Metals	95	105

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

2.3.15.1(b) Mass Calibration and Resolution Checks in the Mass Regions of Interest. The mass calibration and resolution parameters are required criteria which must be met prior to any samples being analyzed. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value. The resolution must also be verified to be less than 0.9 amu full width at 10 percent peak height.

2.3.15.2 INTERNAL STANDARDS (IS)**.** An appropriate internal standard is required for each analyte determined by ICP-MS. The internal standards aid in quantitation of detected analytes and in identifying when physical or chemical interferences are present in samples.

Generally, an internal standard should be no more than 50 amu removed from the analyte. Recommended internal standards are ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{165}Ho, and ^{209}Bi. The lithium internal standard should have an enriched abundance of ^{6}Li, so that interference from lithium native to the sample is minimized. Other elements may need to be used as internal standards when samples contain

significant amounts of the recommended internal standards. The internal standards must be added to the calibration standards, calibration blanks, and preparation blanks as well as to samples and duplicates.

2.3.15.2(a) IS Peak Intensities - Field Samples**.** The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard fails to fall between 30 and 120 percent of the intensity of that internal standard in the initial calibration standard, the following procedure is followed. The sample must be diluted fivefold (1 + 4) and reanalyzed with the addition of appropriate amounts of internal standards. This procedure must be repeated until the internal-standard intensities fall within the prescribed window.

TABLE 14

ICP/MS Linear Range Peak Intensity Control Limits for Field Samples αΩ

Inorganic Species	% of Internal Standard Peak Intensity in Initial Calibration Standard	
	Low Limit	High Limit
Metals	30	120

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

2.3.15.2(b) IS Peak Intensities - QC Samples**.** The intensity levels of the internal standards for the calibration blank and instrument check standard must agree within ± 20 percent of the intensity level of the internal standard of the original calibration solution. If they do not agree, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.

TABLE 15

ICP/MS Linear Range Peak Intensity Control Limits for QC Samples αΩ

Inorganic Species	% of Internal Standard Peak Intensity in Initial Calibration Standard	
	Low Limit	High Limit
Metals	80	120

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

2.3.15.3 RINSE BLANK. In addition to preparation and calibration blanks, ICP/MS analysis requires a third type of blank, a rinse blank. The rinse blank consists of 1 to 2 percent HNO_3 (volume/volume) in reagent water. It is used to flush the system between all samples and samples.

2.3.16 Inorganic Corrective Actions

Whenever an analytical procedure is "out-of-control"[23], the problem must be found, corrected and the analysis repeated (which may require redigestion) for all affected samples. It should be noted that for MS/MSD and method blanks, all affected samples would include any sample that was prepared in the same batch with the out-of-control MS/MSD or blank. The analytical procedure is out-of-control:

1. Whenever the absolute value of the method blank results exceeds the detection limit;

2. Whenever matrix spikes, surrogates, laboratory control samples, reference standards, or other laboratory fortified samples results fall outside control limits;

3. Whenever matrix spike duplicates, laboratory duplicates, or matrix duplicate samples results fall outside control limits;

4. Whenever the ICP interference check sample or spike recovery check sample results fall outside control limits; or

5. Whenever the ICP serial dilution analysis falls outside control limits.

6. Whenever the intensity of any ICP/MS internal standard in a field sample falls outside the control limits of 30 and 120 percent of the intensity of that internal standard in the initial calibration standard.[24]

7. Whenever the intensity of the ICP/MS internal standards for the calibration blank and instrument check standard fall outside the control limits of ± 20 percent of the intensity level of the internal standard of the original calibration solution.

When the DQO would not otherwise be met, reanalysis of "out-of-control" samples must be performed for analytical requirements to be confirmed.[25] If the reanalysis is within control

[23]Note: Whenever a quality control sample indicates a biased high result (e.g., high matrix spike recovery), and the sample results are all below detection limits, then reanalysis is not required. However, the laboratory should make every effort to correct the problem for future analyses.

[24]Note: ICP/MS samples out-of-control for internal standard intensity must be diluted fivefold (1+4) prior to reanalysis.

[25]Note: Reanalysis of out-of-control samples may require that the reanalysis be performed past holding time requirements. It is preferred that samples be analyzed or reanalyzed within holding times. But, if that is not possible for reanalysis to be performed within holding time requirements, reanalysis may still need to be performed to meet analytical requirements. If reanalysis is performed past the holding time, both analysis results should be reported. The acceptance of results analyzed beyond holding time requirements should be predicated on project DQOs and threshold requirements, along with the analyst's best judgement. Resampling may be necessary

limits, only the results of the reanalysis should be reported. If QC control/criteria following redigestion and reanalysis still fall outside acceptance limits, then the laboratory should submit the data from both analyses. Distinguish between the initial analysis and reanalysis on all data deliverables.

It should be noted that the above is contingent upon the initial and continuing calibrations being in control. There are no exceptions to meeting the criteria for calibration.

2.4 Quality Assurance/Quality Control for TCLP Extract Analysis

The following QC measures refer to the performance of determinative analyses on the extract generated according to the specifications of SW-846 Method 1311. All control criteria specified in Method 1311 for sample handling, preparation, extraction, and analysis should also be followed.

2.4.1 TCLP Inorganic Parameters QA/QC Requirements

1) A three- point calibration curve must have a correlation coefficient (**r**) of 0.995 or greater. The curve should define the range of the instrument. One point must be at or near the detection limit and one point at the mid-range of the curve.

2) A calibration verification sample should be analyzed for every ten samples, or one per set if the set contains less than ten samples. The control criterion is a percent recovery between 90% and 110%.

3) A calibration blank and a method blank should be analyzed for every ten samples or one per set if the set contains less than ten samples.

4) A duplicate sample should be analyzed for every ten samples or one per set if the set contains less than ten samples. The RPD control criterion is 20%.

2.4.2 TCLP Organic Parameters QA/QC Requirements

1) An initial calibration is required as provided in Sections 2.4 and 2.5 of this chapter.

2) A calibration verification sample as required in Sections 2.4 and 2.5 should be analyzed every 12 hours, or one per sample set if analyzed in less than 12 hours.

3) A method blank is to be analyzed for every ten samples or one per sample set if the set contains less than ten samples.

4) For TCLP analysis, a duplicate sample should be analyzed for every 10 samples or one per set if the set contains less than 10 samples.

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in some cases.

3.0 ORGANIC ANALYSIS[26]

This section provides guidance related to quantitative analysis of organic compounds by chromatographic methods. Guidance for non-specific organic analyses, such as total organic carbon (TOC) and total organic halides (TOX), can be found in Section 2.0.

Analytical chromatography is used to separate target analytes from co-extracted interferences in samples. Determinative chromatographic methods used for analysis of organic compounds can be divided into two major categories: gas chromatography (GC) and high performance liquid chromatography (HPLC). The determinative method identifies and quantifies the target analytes detected in the sample. Prior to performance of the determinative chromatographic method, many samples require extraction or other preparatory treatments. Some samples with complex matrices also require "cleanup" (removal of certain chemical interferents) prior to analysis.

All chromatographic processes achieve separation by passing a mobile phase over a stationary phase. Constituents in a mixture are separated because they partition differently between the mobile and stationary phases and, thus, have different retention times. Compounds that interact strongly with the stationary phase elute slowly (have a long retention time), while compounds that remain in the mobile phase or interact weakly with the stationary phase elute quickly (have a short retention time).

Gas chromatography is the separation technique of choice for organic compounds that can be volatilized without being decomposed or chemically rearranged. This includes most volatile organic and many semivolatile organic analytes of interest in the environmental field. The preferred capillary columns are more efficient than packed columns (produce better separations). "Reverse phase" high performance liquid chromatography is useful for analysis of environmental samples containing analytes of interest that are semivolatile organic compounds, nonvolatile organic compounds, or decompose upon heating.

Determinative methods can be further categorized by the type of detector that is used with the chromatographic technique. Gas chromatography/mass spectrometry (GC/MS) is gas chromatographic analysis in which the detector is a mass spectrometer. Other gas chromatography systems utilize "selective" detectors, such as Photoionization (PID) or Electron Capture (ECD), or "non-selective" detectors, such as Flame Ionization (FID). Reverse phase HPLC systems generally utilize Ultraviolet (UV) detectors; the UV detectors are often used in conjunction with fluorescence detectors for increased sensitivity. HPLC/MS systems can also be used in which a mass spectrometer functions as the detector.

3.1 Method Selection and Optimization

Chromatographic methods can be used to produce data of appropriate quality for the analysis of environmental and waste samples. However, data quality can be greatly enhanced when the analyst understands both the intended use of the results and the limitations of the specific analytical procedures available to produce the data.

[26]Adapted from *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*, U.S. EPA Publication SW-846, 3rd ed., *Final Update II*: Method 8000B (Rev. 2) "Determinative Chromatographic Separations," and Chapter Two (Rev. 3), "Choosing the Correct Procedure," December 1996.

The combination of preparatory, cleanup, and determinative methods selected for analysis should be those most suitable to meet the DQO requirements, taking sample characteristics into account.

3.1.1 Project Objectives, Matrix Types, and Target Analytes

In order to choose the correct combination of methods to comprise the appropriate analytical procedure, the following basic information must be known:

- Project Objective. The intended use of the data should be communicated to the laboratory analyst. The analytical or project objective could affect choice of preparatory and determinative methods. It can also affect the format and detail in which the data is reported, as well as whether concentrations are reported in wet weight or dry weight and in which units of measurement.

- Phase characteristics of the sample. This includes whether the sample is aqueous, soil, sludge, oil, liquid waste, sediment, multiphasic, etc.[27] Different handling procedures, preparatory methods and, sometimes, different determinative methods are used for samples of various phase characteristics.

- Analytes of interest. The nature of the target analytes may dictate special handling, preparation, or analytical techniques.

- Potential interferences. Chemicals (other than the target analytes) known or suspected of being present in the sample that might interfere with analysis or detection, should also be taken into account when selecting a method or determining if sample cleanup is required.

- Detection Limits. Depending on the project objective and intended end use of the data, specific detection limits may be required. It may be intended to compare the target analyte concentrations to risk-based human health or ecological protective levels, drinking or water detection limits, or regulatory limits such as TCLP or Maximum Contaminant Levels (MCLs). If the detection limit exceeds the comparison value, environmental protection or compliance to regulations cannot be determined. Different determinative methods have different levels of sensitivity and should be chosen accordingly. The preparatory or extraction method can also affect the final detection limit.

3.1.2 Project-Specific Factors

Project specific factors can affect the effectiveness and quality of the data as well as the cost of the analytical process. The greater the available information about the site, unit, waste

[27]The phase of the sample is often incorrectly referred to as the sample "matrix." The matrix, in actuality, includes all characteristics and components of the sample. I.e., the matrix includes the substrate containing the analytes of interest (i.e., the material the phase characteristics describe, the analytes of interest (or target analytes), and all other chemicals found in the substrate: naturally occurring species, anthropogenic materials, and contaminants that are not target analytes.

generation process, or contaminant source, the better the selection of analytical process can be.

3.1.2.1 GC/MS OR HPLC/MS. **If the site or waste stream is not well characterized, and especially if large numbers of target analytes are of concern, analysis by GC/MS or HPLC/MS may be the most appropriate and practical**. When there is little information available about the composition of a sample source, such as previous monitoring well data or waste stream characterization, mass spectral identification of analytes leads to fewer false positive results. It also allows for a large number of target analytes to be tested for simultaneously.

However, unmodified, the mass spectral methods may not be able to achieve the detection limits required by the project objectives. When lower detection limits are required, it may be desirable to do one of the following :

(i) Use GC methods utilizing detection other than mass spectral (MS);
(i) Use HPLC methods utilizing detection other than MS; *Or*
(ii) Provide a variation or modification to the mass spectral method to maximize sensitivity (i.e., to lower detection, quantitation, or reporting limits).

Whenever a method is modified or varied, the resulting procedure should be validated to demonstrate that its performance satisfies the analytical requirements of the specific application for which it is being used. Such demonstrations should be performed using the procedures outlined in *SW-846* Method 8000B (Revision 2, December 1996), Sections 8.2 through 8.5, and *SW-846* Chapter One. This process can be documented using the EPA Performance Based Measurement System draft generic checklist for Initial Demonstration of Method Performance (attached).

3.1.2.2 METHODS USING DETECTION OTHER THAN MS. **GC and HPLC methods using detectors other than MS (such as ECD or PID for GC, or UV for HPLC) are inherently more sensitive than mass spectral methods.** However, these GC methods may present serious difficulties when used for site investigations in which the target analytes are unknown, or in which there are a large number of target analytes, or where there are many interferents, especially if the interfering compounds are at high concentrations. Some of the resulting problems may include: co-elution of target analytes, false negatives due to retention time shifts, and false positives and quantitation errors due to co-eluting non-target sample components. **When such problems occur, the risk of false positive results may be minimized by confirming the results through a second analysis with a dissimilar detector or chromatographic column.**

In contrast, chromatographic methods employing detectors other than MS may be appropriate for remediation activities where the analytes of concern are known, of limited number, and of significantly greater concentration than potentially interfering materials. **When the analytes of concern are limited in number and are all amenable for analysis by the same GC method, it will also be generally less expensive than a mass spectral method.**

Depending on project-specific objectives, it may sometimes be desirable to modify non-MS chromatographic methods to increase sensitivity or optimize

chromatographic conditions for the analytes of concern. Approaches and procedures are similar to those for chromatography using MS detection. (See section 3.1.2.3, below.)

3.1.2.3 INCREASING METHOD SENSITIVITY TO LOWER DETECTION LIMITS. It should be noted that increasing method sensitivity will be influenced by sample types and matrices which vary in analytical behavior. However, some general ways to increase method sensitivity are listed below:

(a) Increase sample size;
(b) Concentrate sample extracts to less than the standard 1 mL volume;
(c) Use of selective ion monitoring (SIM) in mass spectral analysis; (*However, use of SIM may adversely affect compound identification unless multiple ions are monitored for each compound.)*
(d) Use of the most efficient sample preparation technique
(e) Optimize chromatographic conditions for the sample matrix; or
(f) Use an ion trap mass spectrometer or other instrumentation of improved design.

3.1.2.4 SAMPLE PREPARATION AND EXTRACTION EFFICIENCY. The most efficient sample preparation and extraction technique will depend on the target analyte(s) and sample phase and matrix. *SW-846* Chapter Four includes a variety of extraction methods to accommodate various sample characteristics and analytical objectives.

3.1.2.5 OPTIMIZATION OF CHROMATOGRAPHIC CONDITIONS. Columns and conditions described in the analytical methods are those that have been demonstrated to provide optimum separation of all or most target analytes listed in that specific procedure. Most often, those were the columns used during method development and testing. Analysts may change those columns and conditions, provided that they demonstrate performance for the analytes of interest that is appropriate for the intended application.

Possible modifications in GC chromatographic conditions might include:

- increasing column length
- decreasing column diameter
- increasing the capillary film thickness
- modifying column temperature or temperature program

Possible modifications in HPLC chromatographic conditions might include:

- modifying composition or gradient of the solvent mixture
- using packing material with an alternate bonded phase
- using packing material with smaller particle size or pore size
- decreasing column diameter

Whenever a method is modified or varied, the resulting procedure should be validated to demonstrate that its performance satisfies the analytical requirements of the specific application for which it is being used. Such demonstrations should be performed using the procedures outlined in *SW-846* Method 8000B (Revision 2, December 1996), Sections 8.2 through 8.5, and *SW-846* Chapter One. This process

can be documented using the EPA Performance Based Measurement System draft generic checklist for Initial Demonstration of Method Performance (attached).

3.1.2.6 DILUTION OF SAMPLES. When high concentrations of target analytes are present that exceed the linear range of the GC/MS system, samples should be diluted and reanalyzed. All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the calibration curve. The results from both the undiluted and diluted sample should be reported, including chromatograms and mass spectra generated.

3.1.3 Precision and Accuracy Studies

The laboratory should be prepared to submit initial demonstration of proficiency, representative precision, and accuracy data for each method or combination of methods to be used when requested. (See SW-846, Method 8000B, Section 8.0).

3.2 Organic Quality Assurance/Quality Control Measures

The quality control measures generally performed for instrumental organic analysis are summarized below, along with the reasons they are necessary. A more detailed outline with recommended control limits is provided in sections 3.3-3.6. Documentation and deliverables requirements are listed in Appendix II.

Initial Demonstration of Proficiency: Each laboratory must demonstrate initial proficiency with each combination of sample preparation and determinative methods that it utilizes, by generating data of acceptable accuracy and precision for a reference sample containing the target analytes in a clean matrix. The laboratory must also repeat this demonstration whenever new staff are trained or significant changes in instrumentation are made. Too accomplish this demonstration, see *SW-846* Method 8000B, Sec. 8.0 and the EPA Performance Based Measurement System draft generic checklists: Initial Demonstration of Method Performance and Continuing Demonstration of Capability (attached).

Chain-of-Custody: A chain-of-custody procedure should be followed and documented to ensure the traceability through shipment and identity, security, and physical integrity of samples upon receipt at the laboratory. A chain-of-custody form should be initiated by the individual(s) taking the sample and surrendered to laboratory staff with the field samples. The laboratory may also choose to use an internal chain-of-custody process.

All samples should be stored in a separate storage area accessible to authorized personnel only. Access to samples must be restricted to authorized personnel at all times. Sample chain-of-custody within the laboratory should be consistent with the security procedures used by EPA-NEIC (National Enforcement Investigations Center) facilities.

Instrument Detection Limit Determination: An IDL determination should be performed on each instrument for each analyte measured prior to any sample analysis on that instrument. The determination should be repeated at least annually and after any significant instrument modifications.

Method Detection Limit Studies: Method Detection Limit Studies must be performed and documented for each analytical method run by the laboratory. A separate detection limit study must be performed for each sample matrix type analyzed and for each instrument used **to run a** particular method. The detection limit studies should be performed annually and whenever an instrument modification occurs, a new instrument is added, or a new sample matrix type is analyzed.

Holding Time Specifications: It is the facility's or their representative's responsibility to ensure that the analyses are performed within the specified time limits. The required time limits for instrumental organic analyses of various matrix types are given in Table 1-Organics. Required time limits for organics analyses of aqueous samples are given in Supplemental Table 1. The holding time clock begins at the moment the sample is taken.

Instrument Tuning: Gas chromatography/mass spectrometry and high performance liquid chromatography/mass spectrometry methods require that the mass analyzer be tuned to maximize the ion abundance of a specific compound prior to proceeding with calibration and analysis. Tuning checks are sometimes referred to as instrument performance checks.

Calibration: The instrument or analytical equipment is calibrated in order to establish an accuracy range within which a known response results from a specific concentration of analyte. Initial calibration delineates the relationship between the concentration of analyte introduced into the instrument and the instrument response.

Calibration Verification: The calibration relationship established during the initial calibration must be verified at periodic intervals. The calibration verification standard (or standards) is analyzed at a specific frequency throughout the analytical run in order to confirm that the instrument has remained in calibration.

Retention Time Windows: Retention time (RT) windows must be established for the identification of target analytes.

Evaluation of Chromatographic Performance: For each 12-hour period during which analysis is performed, the performance of the entire analytical system should be checked. In addition to the quantitative checks accomplished by analysis of QC samples, general chromatogram appearance and instrument operation is assessed. Certain methods also include specific QC checks of column resolution, instrument sensitivity, analyte degradation, or mass calibration at the beginning of a 12-hour analytical shift.

Internal Standard Performance Criteria: Internal Standards are used to adjust area counts for target analytes to account for injection and run condition variations. Internal standard retention times and area counts or response factors are also evaluated to ensure that instrument sensitivity and response are stable throughout the analytical run, and to ensure that measurement of the internal standard is not affected by sample-specific factors such as presence of target analytes, surrogates, and matrix interferences. Even when not explicitly required by the analytical method, use of internal standards can be beneficial for chromatographic methods, especially when low concentrations are being analyzed.

Instrument Blank: The instrument blank, sometimes referred to as the calibration blank, has a twofold purpose. Initially it is used to assess the instrument's or equipment's performance (e.g., instrument noise) without the analyte being present. Secondly, it is used to confirm that there was

no carryover between analyses or that the response has not changed throughout the analysis. The instrument blank is analyzed at the beginning of analysis and at a specific frequency throughout the analysis run.

Method Blank: The method blank, sometimes referred to as the preparation blank, is used to verify that contamination was not introduced into the analyses by sample handling, including the preparation step and sample analysis. The method blank is handled and analyzed in the same manner as the samples. The method blanks are analyzed at a specific frequency throughout the analysis run.

Solvent Blank: Similar to the second purpose listed above for an instrument blank, a solvent blank is an aliquot of pure solvent that may be injected between samples to check for contamination by carryover.

Matrix Spike: An actual sample is spiked before the preparation step with the analyte of interest at a known concentration in order to determine if the sample matrix is interfering with the analyte response. The matrix spike is used to assess the accuracy of the analysis in the actual sample matrix. The matrix spike samples are analyzed at a specific frequency throughout the analysis run.

Matrix Spike Duplicate: A second matrix spike is prepared and analyzed as before in order to confirm that there is consistency in preparation and analysis. The matrix spike duplicate is used to assess analytical precision. The matrix spike duplicates are analyzed at a specific frequency throughout the analysis run.

Duplicate Sample Analysis: A laboratory duplicate sample, also referred to as a matrix duplicate, is prepared and analyzed in order to confirm that there is consistency in preparation and analysis. Analysis of laboratory duplicate samples is used to assess analytical precision. Laboratory duplicate samples are analyzed at a specific frequency throughout the analytical run. Some methods specify or allow analysis of a matrix duplicate in place of a matrix spike duplicate.

Field Duplicate Analysis: A field duplicate sample is collected at a specified frequency during field activities. The field duplicates are treated as independent samples during laboratory processes of preparation and analysis. Analysis of field duplicate samples is used to assess variability introduced by the sampling process and sample matrix homogeneity.

Laboratory Control Sample: The laboratory control sample is sometimes referred to as a quality control check sample, quality control reference sample, or laboratory fortified blank. A clean control matrix (blank) is spiked with the analyte of interest before the preparation step and analyzed in the same manner as the samples to verify that the analytical method is within control. The results of the laboratory control check sample are used to assess (in conjunction with the matrix spike) if poor analytical performance is matrix dependent or an analysis method problem.

Quality Control Check Sample: See Laboratory Control Sample.

Surrogate Recoveries: Surrogate standards (also referred to as system monitoring compounds or surrogate spikes) are compounds similar to the target analytes in chemical composition and behavior that are added to each sample, blank, calibration standard, and QC sample. Surrogate recovery data is used to monitor the effectiveness of the analytical system (performance of the extraction, cleanup, and determinative method) in dealing with each individual sample matrix.

Degradation/Breakdown Standard: For pesticide analysis, a standard is analyzed using specific indicator compounds (e.g. Endrin, DDT) to assess if the chromatography system has a degradation or breakdown problem.

Initial Demonstration of Proficiency: Each analyst should demonstrate initial proficiency with each combination of sample preparation and determinative method he or she is responsible for running, by generating data of acceptable accuracy and precision for a reference sample containing the target analytes in a clean matrix. The demonstration should be repeated when significant changes in instrumentation are made.

A specific method or the data quality objectives for a specific environmental project may require additional control items in order to verify that the analysis was under control at each step.

3.3 Analysis of Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry: QA/QC Operations and Reporting

The holding times and preservative techniques specified in Table 1 - ORGANICS or Table 1 Supplemental should be adhered to based on sample characteristics.

3.3.1 Instrument Tuning

Each GC/MS system must be hardware-tuned for accurate mass assignment, sensitivity, and resolution using the compound specified in the analytical method. The tuning criteria specified in the method must be met, prior to the initial calibration procedure. Tuning must be repeated every 12 hours while analysis continues. Analyses must not begin until the criteria specified in the method are met. All subsequent standards, samples, MS/MSDs, LCSs, and blanks associated with a BFB analysis must use identical mass spectrometer instrument conditions.

For volatile organic analysis, tuning is accomplished using a 5-50 ng injection or purging of 4-bromofluorobenzene (BFB), i.e., a 2-µL injection of the BFB standard. (Note that if a more sensitive mass spectrometer is used to achieve lower detection levels, a BFB standard more dilute than the usual 25 ng/ L concentration may be required.) Recommended tuning criteria are listed in *TABLE 16*.

3.3.2 Initial Calibration

Initial calibration must be performed and documented for each instrument used to analyze samples. Initial calibration of volatile organic target compounds should be performed using a minimum of 5 concentrations. The concentration range of the calibration standards should bracket the concentrations of target compounds expected to be seen in the field samples and should be wide enough to meet the project DQOs. At least one standard should be at a concentration as low or lower than regulatory or health protective levels to which sample concentrations will be compared. The remaining standards should correspond to the range of concentrations found in typical samples but should not exceed the working range of the GC/MS system. Project DQOs requiring very low detection limits (e.g. risk assessment) may require specialized calibration and analytical procedures, such as preparation of lower concentration standards to 25 L volume (and purging 25 L sample) rather than using 5 L

volumes.[28]

TABLE 16
Recommended BFB Tuning Criteria for VOC Analysis αΩ

m/z	Required Intensity (relative abundance)
50	15 to 40% of m/z 95
75	30 to 60% of m/z 95
95	**Base peak, 100% relative abundance**
96	5 to 9% of m/z 95
173	Less than 2% of m/z 174
174	Greater than 50% of m/z 95
175	5 to 9% of m/z 174
176	Greater than 95% but less than 101% of m/z 174
177	5 to 9% of m/z 176

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

If an analyte saturates at the highest standard concentration level, and the GC/MS system is calibrated to achieve a detection sensitivity consistent with the project DQOs, the laboratory should document it in the report narrative. In this instance, the laboratory should calculate the results based on a four-point initial calibration *for the specific analyte* that saturates.

The target analytes are quantitated through the calculation of a response factor (RF). A RF is a measure of the relative instrument response of a target analyte as compared to the instrument response of its internal standard. It is calculated as the ratio of the peak area of the target compound in the sample to the peak area of the internal standard in the sample:

$$RF = \frac{A_s - C_{is}}{A_{is} - C_s}$$

where: A_s = Peak area of the analyte or surrogate
A_{is} = Peak area of the internal standard
C_s = Concentration of the analyte or surrogate
C_{is} = Concentration of the internal standard

[28]If project DQOs required detection limits lower than 1 part per billion (ppb), it may be necessary to use selected ion monitoring (SIM) techniques or, for aqueous samples, to follow GC/MS Method 524.2 procedures. Another alternative would to be perform analysis by a GC method that does not use MS detection.

The internal standard selected for quantitation (i.e., calculation of the response factor) of a particular target analyte should be the internal standard that has a retention time closest to the analyte being measured. The target analytes should be quantitated using the base peak ion (most intense ion, also referred to as primary ion) from the appropriate internal standard. If there are sample interferences with the primary ion, the next most intense ion should be used as the quantitation ion. If this occurs, document the reasons in the report narrative.

Initial calibration of a GC/MS system is performed upon installation of an instrument, prior to beginning analysis of a sample case for an environmental project, whenever corrective action is taken on the system which may change or affect the initial calibration criteria (ion source cleaning or repair, column replacement, etc.), or if the continuing calibration (calibration verification) acceptance criteria have not been met.

3.3.2.1 VALIDATION OF INITIAL CALIBRATION

A system performance check must be made and documented for the initial calibration to be considered valid. The following criteria must be met:

(A) The mean response factors (RFs) for the volatile System Performance Check Compounds (SPCCs) must be no lower than the minima indicated in *TABLE 17*. Specific compounds that are especially susceptible to certain analytical problems were selected to be the SPCCs. They are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system.

(B) The relative standard deviation (RSD) of the response factors for each individual volatile Calibration Check Compound (CCC) must be less than or equal to 30%. The purpose of the CCCs is to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may indicate system leaks or reactive sites in the column. The CCCs are listed in *TABLE 17*.

(C) The RSD of the response factors for all other target analytes should be less than or equal to 15%.[29]

(D) Retention times should be evaluated for all target analytes. The relative retention times of each target analyte in each calibration standard should agree within 0.06 relative retention time units.

(E) Good GC performance should be indicated on the total ion chromatogram. Good column performance will produce symmetrical peaks with minimum tailing for most compounds. If peaks are unusually broad, or if there is poor resolution between peaks, corrective action is required before analysis can begin.

(F) Adequate MS sensitivity should be demonstrated by the calibration data generated. The GC/MS identification software should be able to recognize a GC peak in the appropriate retention time window for each of the compounds in the calibration solution and make good tentative identifications. If fewer than 99% of the compounds are recognized, system maintenance is required.

[29]SW-846 Method 8260B requires a 15% RSD. (See SW-846 3rd ed. Final Update III page 8260B-18.) Water method 524.2 and the CLP GC/MS VOA procedure specify a linearity criterion of 20% RSD.

The RSD is calculated from the mean and standard deviation of the response factors for the five concentration measurements of each analyte:

$$RSD = \frac{SD}{\overline{RF}} \times 100$$

where: $\overline{RF}$ = mean RF for that compound from the initial calibration at 5 concentrations
SD = Standard Deviation for that 5 RFs for the compound from the initial calibration

The standard deviation is calculated as a sample standard deviation (not a population standard deviation):

$$SD = \sqrt{\frac{\sum_{i=1}^{n} \left(RF_i - \overline{RF}\right)^2}{n-1}}$$

where: RF_i = RF for each of the 5 calibration standards from the initial calibration for that compound
$\overline{RF}$ = mean RF of the 5 concentrations from the initial calibration for that compound
n = Number of calibration standards (e.g. 5)

The criteria listed in *TABLE 17* must be met for the initial calibration to be valid. Only after these criteria are met can sample analysis begin:

- If the minimum mean response factor criterion for any SPCC is not met, the system must be evaluated and corrective action must be taken before beginning or continuing sample analysis.
- If an RSD of greater than 30% is measured for any CCC, then corrective action to eliminate a system leak and/or column reactive sites is necessary before reattempting calibration.
- If the RSD of any non-CCC analyte is greater than 15%, a new initial calibration should be performed.[30]

[30]Alternatively, rather than reattempting linear calibration, it may be appropriate to use a non-linear calibration model. The non-linear option should be reserved for appropriate circumstances, such as the need to achieve low detection limits. Non-linear calibration may not be used to compensate for detector saturation at higher concentrations or to avoid proper instrument maintenance.

TABLE 17

Initial Calibration Criteria for VOC Analysis αΩ

Analyte Type	Compound	Minimum Mean RF	Maximum RSD
SPCC	Chloromethane	0.10	15%
SPCC	1,1-Dichloroethane	0.10	15%
SPCC	Bromoform	0.10	15%
SPCC	Chlorobenzene	0.30	15%
SPCC	1,1,2,2-Tetrachloroethane	0.30	15%
CCC	1,1-Dichloroethene	—	30%
CCC	Chloroform	—	30%
CCC	1,2-Dichloropropane	—	30%
CCC	Toluene	—	30%
CCC	Ethylbenzene	—	30%
CCC	Vinyl chloride	—	30%
ALL OTHER TARGET ANALYTES		—	15%

Additional Calibration Criteria Applicable to All Compounds (Target and QC)	
RT Evaluation	Agreement within ± 0.06 relative retention time units for RTs of each target analyte among the 5 calibration standards.
GC Performance	Symmetrical peaks, minimum tailing, good resolution
MS Sensitivity	99% (minimum) target compound peaks recognized and identified in appropriate retention time window

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3.3.3 Calibration Verification

The calibration relationship established during the initial calibration must be verified at periodic intervals. Calibration verification consists of the following three steps that should be performed at the beginning of each 12-hour analytical shift. A minimum of one calibration verification should be reported per sample set, even if the set is completed in fewer than twelve hours of analysis time. The calibration verification steps include:

(1) BFB is analyzed and results compared to the criteria in the method (or Table 16) to verify mass calibration and tuning. The criteria must be met prior to further analysis.

(2) A calibration verification standard at a concentration near the midpoint of the calibration range is analyzed and assessed for the following criteria. The calibration standard should contain all target compounds, surrogates, and internal standards.

(A) System performance check. Each SPCC in the calibration verification standard must meet the minimum response factor listed in Table 17.If the minimum response factors are not met, the system must be evaluated and corrective action taken before beginning or continuing sample analysis.

(B) Calibration validation: The response factors for the CCCs in the calibration verification standard are compared to the mean response factors determined in the initial calibration through a percent difference (%D) calculation.[31] The %D is calculated as follows:

$$\frac{RF_V - \overline{RF}}{\overline{RF}} \; x \; 100$$

where: RF_V = the response factor for the verification standard, and
$\overline{RF}$ = the mean response factor from the initial calibration.

The %D criteria must meet the criteria in *TABLE 18* for the initial calibration to be considered valid. If the CCCs are not in or added to the list of target analytes for the project, the %D criteria should be applied to all analytes.

If the criteria in *TABLE 18* are not met for any one compound, then corrective action must be taken prior to the analysis of samples. If attempts to correct the problem are unsuccessful, a new initial five-point calibration must be performed.

(C) Calibration Standard Internal Standard Check: Internal standards criteria for the calibration verification standard must be evaluated during or immediately after data acquisition. The retention time for any internal standard in the calibration verification standard must not change by more than 30 seconds from the RTs of the internal standards in the mid-range concentration standard of the most recent initial calibration sequence. The peak area counts for the internal standards in the calibration verification standard must change by less than a factor of 2 (-50% to +100%) from the area counts for the internal standard peaks in the mid-range concentration standard of the most recent initial calibration sequence.

[31] RF %D is calculated when the calibration model used is average response factor. If a non-linear regression fit model is used, percent drift is calculated instead. See SW-846 Method 8000B.

If either of these criteria are not met, the mass spectrometer must be inspected for malfunctions, and corrections must be made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required. Corrections should be documented in the case narrative. Internal standard RT and area count data should be reported for both analyses (before and after corrective action).

TABLE 18

Response Factor %D Calibration Verification Criteria for VOC Analysis αΩ

Analyte Type	Compound	Maximum %D
CCC	**1,1-Dichloroethene**	**20%**
CCC	**Chloroform**	**20%**
CCC	**1,2-Dichloropropane**	**20%**
CCC	**Toluene**	**20%**
CCC	**Ethylbenzene**	**20%**
CCC	**Vinyl chloride**	**20%**
Alternatively, if CCCs are not in analyte list: **ALL TARGET ANALYTES**		**20%**

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

(3) A method blank should be analyzed after the calibration standard to assure that the total system (introduction device, transfer lines, and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to ensure that the contamination is not a result of carryover from standards or samples.

3.3.4 Blanks

A method blank is an organic-free water sample taken through the entire preparatory and analytical procedure step by step, including all the reagents and solvents in the quantity required by the method. The organic-free water used must meet the specific method requirements. Prior to being subjected to the method procedure, interferents should not be observed in the water at the method detection limit of the compounds of interest.

(1) Frequency. For volatile organic compounds analyzed by the purge-and-trap method, the preparation is equivalent to the analysis. Therefore, one purge-and-trap method blank must be analyzed with each group of samples analyzed on the same instrument during the same analytical shift. At a minimum, this frequency should be one method blank per 12-hour shift per instrument.

(2) Control Criteria. Analysis of a volatile method blank should meet the following criteria:

(A) Methylene chloride, acetone, toluene, and 2-butanone (common laboratory contaminants) should be present at a concentration no greater than 5 times the estimated quantitation limit (EQL).

(C) Concentrations of target analytes observed in the method blank should be no higher than the highest of:

(i) The laboratory's MDL for the analyte;
(ii) 5% of the regulatory limit for that analyte (applicable only if the sample results will be compared to that regulatory limit); or
(iii) 5% of the measured concentration in the sample.

(3) Failure of control criteria. If any laboratory method blank exceeds these criteria, the laboratory should take corrective action. The source of the contamination should be located, the contaminant concentration should be reduced, and all relevant information should be documented. All samples processed with the contaminated method blank should be re-extracted/repurged and reanalyzed.

(4) Results and reporting. The laboratory should report results of all volatile method blank analyses. However, the laboratory should not subtract the results of the method blank from those of any associated samples.

3.3.5 Matrix Spike and Matrix Spike Duplicate (or Matrix Spike and Unspiked Duplicates)

To document the effect of the matrix, at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair (MS/MSD) should be analyzed. In matrix spike/matrix spike duplicate analysis, predetermined quantities of stock solutions of target analytes are added to a sample matrix prior to sample extraction and analysis. Samples are split into duplicates, spiked and analyzed. Percent recoveries are calculated for each of the analytes detected and used to assess bias due to sample matrix effects. The relative percent difference (RPD) between the split samples is calculated and used to assess analytical precision.

If the option to analyze a matrix spike and unspiked duplicates is chosen, the single matrix spike is used to assess bias, and the RPD of unspiked split samples is used to assess precision. However, if unspiked duplicates are used in place of the MSD, it may be difficult to assess the precision of target analytes present at low concentrations or below detection limits. Unspiked duplicates should only be used if samples are expected to contain target analytes at concentrations at least an order of magnitude higher than the detection limit. If samples are not expected to contain target analytes (or are expected to contain target analytes at concentrations near the detection limit), the laboratory should use a matrix spike and matrix spike duplicate pair.

(1) MATRIX SPIKE. The matrix spike analysis is designed to provide information about the effect of the sample matrix on the preparation and measurement methodology. The matrix spike (and MSD, if applicable) is a measure of the bias attributed to sample matrix effects, not just laboratory process effects on phase or concentration characteristics. The sample matrix includes the target and non-target analytes present in the sample or group of samples: naturally occurring compounds as well as contaminants. Therefore, the spiked sample must be from the same project as the case of field samples. **If the spiked sample is not from the same project as the field samples, matrix effects cannot be determined and sample results must be qualified as estimated.**

At least one MS should be performed on each group of samples of a similar matrix type from the same project (e.g., water, sludges, soil) for each group of 10 (or fewer) samples received per project. However, it is not necessary to spike samples when the concentration of the analyte in the unspiked sample exceeds 0.1%.

(A) Selection of sample to be spiked. For many projects, DQO requirements may dictate that the sampling team select the sample to be spiked based on a pre-site visit evaluation. The rationale for specifying a specific sample to be spiked should be documented by the facility. This does not preclude the laboratory from spiking a sample of its own selection in addition to those samples provided by the facility. **However, samples identified as field blanks may not be spiked.**

(B) Compounds to be spiked . Matrix spiking solutions should be prepared from volatile organic compounds which are representative of the compounds being investigated. It is highly recommended that the MS/MSD be prepared using all target analytes in order to accurately interpret matrix effects on sample results.

At a minimum (if the project target analytes include no polar compounds), the matrix spike should include 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. If any of the target analytes are polar compounds, it will be necessary to spike polar analytes in addition to the minimum five. % Recoveries and RPDs (if applicable) should be reported for all analytes spiked.

The matrix spiking solutions should not be prepared from the same standards as the calibration standards. However, the same spiking standard prepared for the matrix spike may be used for the LCS.

(C) Spike concentrations. The concentration of the stock spiking solution and the final concentration of the spike in the sample will be specified in the individual methods of analysis and generally should be followed. However, the concentration may require adjustment to meet project DQOs. For example, if a method modification or a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute matrix spiking solutions may be required.

(D) Control limits. Recommended control limits for the MS (and MSD, if applicable) % Recovery are listed in *TABLE 19*. The % Recovery for each

component is calculated as follows. When the concentration of the spiked analyte is less than the detection limit in the unspiked sample, use SR = 0 for purposes of calculating % R:

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

Where: SSR = Spiked Sample Result
SR = Sample Result (prior to spiking)
SA = Spike Added

(2) MS/MSD OR UNSPIKED MATRIX DUPLICATE PAIR. At least one MSD or one unspiked duplicate should be performed on each group of samples of a similar matrix type from the same project (e.g., water, sludges, soil) for each group of 10 (or fewer) samples received per project. To assess precision, the Relative Percent Difference is defined by the following equation. MS/MSD and matrix duplicate RPDs should be reported. Recommended RPD control limits are listed in *TABLE 19*.

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

Where: D_1 = %R Value for First Duplicate (unspiked sample or MS)
D_2 = %R Value for Second Duplicate (unspiked dup. or MSD)

TABLE 19A
MS/MSD and Matrix Duplicate Control Criteria for VOC Analysis αΩ

Matrix:	**Water**		**Other Matrices**	
Compound	**MS/MSD Spike %Recovery**	**MS/MSD or Duplicate RPD**	**MS/MSD Spike %Recovery**	**MS/MSD or Duplicate RPD**
1,1-Dichloroethene	61-145	**14**	59-172	22
Trichloroethene	71-120	**14**	62-137	2**4**
Benzene	76-12**7**	**11**	66-142	21
Toluene	76-125	**13**	59-139	21
Chlorobenzene	75-130	**13**	60-133	21
ALL OTHER ANALYTES	70-130	20	60-140	30

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3.3.6 Field Duplicate Sample Analysis

At least one field duplicate sample should be collected for every matrix sampled per sampling event. If large numbers of samples are collected, it is recommended that at least one field duplicate pair be collected for every 20 samples collected. Field duplicates should be treated as independent samples for preparation, analysis, and reporting purposes.

The RPD for each analyte detected should be calculated and reported in the QC report. The RPD is calculated in the same way for matrix duplicates and laboratory replicates as is indicated above for matrix spike duplicates. If the RPD exceeds the control limits listed in *TABLE 19B*, data should be qualified as estimated.

TABLE 19B
Recommended Control Limits for Field Duplicate Sample Analysis RPD

Compounds	Aqueous Samples RPD	Soil, Sludge, Sediment, Oil, & Waste Samples RPD
ALL TARGET ANALYTES	± 25 %	± 40 %

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3.3.7 Analysis of Surrogates

The recommended surrogates for GC/MS analysis of VOCs are toluene-d_8, 4-bromofluorobenzene, 1,2-dichloroethane-d_4, and dibromofluoromethane. Other compounds may be used as surrogates, depending upon the analysis requirements. Every blank, standard, environmental sample (including matrix spike/matrix spike duplicate and matrix duplicate samples) should be spiked with surrogate compounds prior to purging or extraction.

Surrogates should be spiked into samples as directed in the appropriate analytical methods. The concentration of the surrogate spiking solution and final concentration of surrogate in the samples should be appropriate to the project DQOs. For example, if a more sensitive mass spectrometer or method modification is used to achieve lower detection limits, a spiking solution more dilute than the usual 5-25 μg/mL and a final surrogate concentrations lower than 50 μg/L may be required.

(1) Control criteria for surrogate recoveries. Surrogate spike recoveries should not exceed the control limits listed in the analytical method or developed by the laboratory for samples within the quantitation limits before dilution. The control limits used should be specified in the project QAPP. Recommended control criteria for volatile surrogate recoveries are listed in Table 20.

Surrogate recoveries are calculated as:

$$\text{Recovery (\%)} = \frac{\text{Concentration (or amount) found}}{\text{Concentration (or amount) added}} \times 100$$

TABLE 20

Recommended Surrogate Spike Control Criteria for VOC Analysis αΩ

Matrix:	**Water**	**Soil & Other Matrices**
Compound	**Surrogate Spike %Recovery**	**Surrogate Spike %Recovery**
Toluene-d_8	88-110	81-117
4-Bromofluorobenzene	86-115	74-121
1,2-Dichloroethane-d_4	76-114	80-120
Dibromofluoromethane	86-118	80-120

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(2) Corrective actions for surrogate recovery problems. The laboratory should take the actions listed below if recovery of any surrogate compound is outside of the surrogate recovery limits required in the project QAPP .

(A) Check calculations to ensure that there are no errors; check internal standard and surrogate spiking solutions for degradation, contamination, etc. Examine chromatograms for interfering peaks and integrated peak areas. Also, check instrument performance.

(B) If the above steps fail to identify the problem, then reanalyze the sample or extract.

(C) If, after the above steps are followed, surrogate recoveries still do not meet control criteria and the sample was a soil extracted with methanol, then re-extract and reanalyze the sample.

(D) If re-extraction and/or reanalysis of the sample does not solve the problem (i.e., surrogate recoveries are outside the requirements for both analyses), then submit the surrogate spike recovery data and the sample data from both analyses. Distinguish between the initial analysis and the reanalysis on all data deliverables. (See Section 3.5, Corrective Action for Organic Analysis by GC/MS, for additional information.)

(3) Dilution of surrogate response. Some samples may require dilution in order to bring one or more target analytes within the calibration range or to overcome significant interferences with some analytes. This may result in the dilution of the surrogate responses to the point that the recoveries can not be measured. If the surrogate recoveries are available from a less-diluted or undiluted aliquot of the sample or sample extract, those recoveries may be used to demonstrate that the surrogates were within the QC limits, and no further action is required. However, the results of both the diluted and undiluted (or less-diluted) analyses should be provided to the data user.

Although the surrogates may be diluted out of certain sample extracts, their retention times in the calibration standards may be useful in tracking retention time shifts. Whenever the observed retention time of a surrogate is outside of the established retention time window, the analyst is advised to determine the cause and correct the problem before continuing analyses

3.3.8 Internal Standards

All samples (including matrix spike/matrix spike duplicate and matrix duplicate samples), standards, and blanks must be spiked with the internal standards.

(1) Choosing internal standards. The recommended internal standards are fluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4. Depending on the project target analytes, sample matrix, the technique used for introduction of the compounds into the GC/MS system (e.g., purge-and-trap, direct injection, closed-system vacuum distillation, or equilibrium head space), it may be appropriate to use other compounds as internal standards. Other compounds may be used as long as they have retention times similar to the target compounds being detected by GC/MS. The compounds chosen as internal standards should permit most components of interest in a chromatogram to have retention times of 0.80 - 1.20, relative to one of the internal standards.

(2) Control criteria for internal standards. Area counts of the internal standard peaks in the samples (environmental and QC) must be within 50-200% of the area of the corresponding peak in the 12-hour calibration verification standard. The retention times for each internal standard in the sample must not vary by more than 30 seconds. If these criteria are not met, the analysis of all affected samples should be repeated.

(3) Assignment of internal standards for quantitation. The internal standard selected for quantitation of a particular target compound should be the internal standard that has a retention time closest to the retention time of the analyte being measured. Table 21 lists the possible assignment of target compounds to the recommended internal standards for quantitation.

TABLE 21

Volatile Internal Standards with Corresponding Analytes Assigned for Quantitation αΩ

Bromochloromethane	1,4-Difluorobenzene	Chlorobenzene-d_5
Acetone	Benzene	Bromobenzene
Acetonitrile	Bromodichloromethane	4-Bromofluorobenzene *(surr.)*
Acrolein	Bromoform	Chlorobenzene
Acrylonitrile	2-Butanone	2-Chlorotoluene
Bromochloromethane	Carbon tetrachloride	4-Chlorotoluene
Bromomethane	Chlorodibromomethane	Ethylbenzene
Carbon disulfide	2-Chloroethyl vinyl ether	Ethyl methacrylate
Chloroethane	Dibromomethane	2-Hexanone
Chloroform	1,2-Dichloropropane	Isopropylbenzene
Chloromethane	1,3-Dichloropropane	4-Methyl-2-pentanone
Dichlorodifluoromethane	cis-1,3-Dichloropropene	n-Propylbenzene
1,1-Dichloroethane	trans-1,3-Dichloropropene	Styrene
1,2-Dichloroethane	1,1,1-Trichloroethane	1,1,2,2-Tetrachloroethane
1,2-Dichloroethane-d_4 *(surr.)*	1,1,2-Trichloroethane	Tetrachloroethene
1,1-Dichloroethene	Trichloroethene	Toluene
cis-1,2-Dichloroethene	Vinyl acetate	Toluene-d_8 *(surr.)*
trans-1,2-Dichloroethene		1,2,3-Trichloropropane
2,2-Dichloropropane		Xylenes
Iodomethane		
Methylene chloride		
Trichlorofluoromethane		
Vinyl chloride		

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3.3.9 Laboratory Control Sample

A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the all the target analytes at the same concentrations as the matrix spike, and the % recoveries are calculated. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. LCS percent recoveries should be reported.

TABLE 21

Recommended Laboratory Control Sample %R Criteria for Organic Analysis [αΩ]

Matrix:	**Water**	**Soil & Other Matrices**
Compound	**LCS %Recovery**	**LCS %Recovery**
ALL TARGET ANALYTES	70-130	60-140

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3.4 Analysis of Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry: QA/QC Operations and Reporting

GC/MS analysis can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and are sufficiently volatile and thermally stable for gas chromatography without derivatization. Such compounds include polynuclear aromatic hydrocarbons (PAHs), chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols.

In most cases, GC/MS analysis is not appropriate for the *quantitation* of multicomponent analytes (e.g. polychlorinated biphenyl compounds (PCBs), toxaphene, chlordane, etc.), because of limited sensitivity for those analytes. When these analytes have been identified by another technique, GC/MS analysis is appropriate for *confirmation* of the presence of these analytes when concentration in the extract permits. See Section 3.6 on Gas Chromatography/Electron Capture Detector (GC/ECD) for guidance on quantitative analysis of multicomponent analytes.

Samples must be extracted prior to analysis. Based on sample matrix characteristics, follow requirements in appropriate preparation techniques (including sample cleanup if applicable). Preservative techniques specified in Table 1 - ORGANICS or Table 1 Supplemental should be adhered to based on sample characteristics. Holding time requirements for both samples and extracts should be met.

3.4.1 Instrument Tuning

Each GC/MS system must be hardware-tuned for accurate mass assignment, sensitivity, and resolution using the compound specified in the analytical method. The tuning criteria specified in the method must be met prior to the initial calibration procedure. Tuning must be repeated every 12 hours while analysis continues. Analyses must not begin until the criteria

specified in the method are met. All subsequent standards, samples, MS/MSDs, LCSs, and blanks associated with a DFTPP analysis must use identical mass spectrometer instrument conditions.

For semivolatile organic analysis, a 50 ng injection of decafluorotriphenylphosphine (DFTPP) is used. (Note that if a more sensitive mass spectrometer is used to achieve lower detection levels, a DFTPP solution more dilute than the usual 50 ng/μL concentration may be required.) Recommended tuning criteria are listed in Table 22, below.

TABLE 22
Recommended DFTPP Tuning Criteria for SVOC Analysis αΩ

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	< 2% of mass 69
69	< 2% of mass 69
127	40-60% of mass 198
197	< 1% of mass 198
198	**Base peak, 100% relative abundance**
199	5-9% of mass 198
275	10-30% of mass 198
365	> 1% of mass 198
441	Present, but less than mass 443
442	> 40% of mass 198
443	17-23% of mass 442

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3.4.2 Initial Calibration

Initial calibration must be performed and documented for each instrument used to analyze samples. Initial calibration of volatile organic target compounds should be performed using a minimum of 5 concentrations. The concentration range of the calibration standards should bracket the concentrations of target compounds expected to be seen in the field samples and should be wide enough to meet the project DQOs. At least one standard should be at a concentration as low or lower than regulatory or health protective levels to which sample concentrations will be compared. The remaining standards should correspond to the range of concentrations found in typical samples but should not exceed the working range of the

GC/MS system. Project DQOs requiring detection limits below the normal range of electron impact mass spectrometry (e.g. risk assessment) may require specialized calibration and analytical procedures. For example, the use of selected ion monitoring (SIM) is acceptable. However, SIM may provide a lesser degree of confidence in the compound identification unless multiple ions are monitored for each compound.

If an analyte saturates at the highest standard concentration level, and the GC/MS system is calibrated to achieve a detection sensitivity consistent with the project DQOs, the laboratory should document it in the report narrative. In this instance, the laboratory should calculate the results based on a four-point initial calibration *for the specific analyte* that saturates.

The target analytes are quantitated through the calculation of a response factor (RF). A RF is a measure of the relative instrument response of a target analyte as compared to the instrument response of its internal standard. It is calculated as the ratio of the peak area of the target compound in the sample to the peak area of the internal standard in the sample:

$$RF = \frac{A_s - C_{is}}{A_{is} - C_s}$$

where: A_s = Peak area of the analyte or surrogate
A_{is} = Peak area of the internal standard
C_s = Concentration of the analyte or surrogate
C_{is} = Concentration of the internal standard

The internal standard selected for quantitation (i.e., calculation of the response factor) of a particular target analyte should be the internal standard that has a retention time closest to the analyte being measured. The target analytes should be quantitated using the base peak ion (most intense ion, also referred to as primary ion) from the appropriate internal standard. If there are sample interferences with the primary ion, the next most intense ion should be used as the quantitation ion. If this occurs, document the reasons in the report narrative.

Initial calibration of a GC/MS system is performed upon installation of an instrument, prior to beginning analysis of a sample case for an environmental project, whenever corrective action is taken on the system which may change or affect the initial calibration criteria (ion source cleaning or repair, column replacement, etc.), or if the continuing calibration (calibration verification) acceptance criteria have not been met.

3.4.2.1 VALIDATION OF INITIAL CALIBRATION. A system performance check must be made and documented for the initial calibration to be considered valid. The following criteria must be met:

(1) The mean response factors (RFs) for the volatile System Performance Check Compounds (SPCCs) must be no lower than the minima indicated in *TABLE 23*. Specific compounds that are especially susceptible to certain analytical problems were selected to be the SPCCs. They are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system.

(2) The relative standard deviation (RSD) of the response factors for each individual volatile Calibration Check Compound (CCC) must be less than or equal to 30%. The purpose of the CCCs is to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may indicate system leaks or reactive sites in the column. The CCCs are listed in *TABLE 23*.

(3) The RSD of the response factors for all other target analytes should be less than or equal to 15%.[32]

(4) Retention times should be evaluated for all target analytes. The relative retention times of each target analyte in each calibration standard should agree within 0.06 relative retention time units.

(5) Good GC performance should be indicated on the total ion chromatogram. Good column performance will produce symmetrical peaks with minimum tailing for most compounds. If peaks are unusually broad, or if there is poor resolution between peaks, corrective action is required before analysis can begin.

(6) Adequate MS sensitivity should be demonstrated by the calibration data generated. The GC/MS identification software should be able to recognize a GC peak in the appropriate retention time window for each of the compounds in the calibration solution and make good tentative identifications. If fewer than 99% of the compounds are recognized, system maintenance is required.

The RSD is calculated from the mean and standard deviation of the response factors for the five concentration measurements of each analyte:

$$RSD = \frac{SD}{\overline{RF}} \; x \; 100$$

where: $\overline{RF}$ = mean RF for that compound from the initial calibration at 5 concentrations
SD = Standard Deviation for that 5 RFs for the compound from the initial calibration

[32]SW-846 Method 8270C requires a 15% RSD, except that the criterion is 30% for CCCs. (See SW-846 3rd ed. Final Update III page 8270C-16.) Water method 525.2 specifies a linearity criterion of 30% RSD for all analytes, and the CLP GC/MS SVOA procedure specifies 20.5% for most analytes.

The standard deviation is calculated as a sample standard deviation (not a population standard deviation):

$$SD = \sqrt{\frac{\sum_{i=1}^{n} \left(RF_i - \overline{RF} \right)^2}{n-1}}$$

where: RF_i = RF for each of the 5 calibration standards from the initial calibration for that compound

$\overline{RF}$ = mean RF of the 5 concentrations from the initial calibration for that compound

n = Number of calibration standards (e.g. 5)

The criteria listed in Table 23 must be met for the initial calibration to be valid. Only after these criteria are met can sample analysis begin .

- If the minimum mean response factor criterion for any SPCC is not met, the system must be evaluated and corrective action must be taken before beginning or continuing sample analysis. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

- If the RSD of any CCC is greater than 30%, then the chromatographic system is too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the initial calibration procedure.

- If the RSD of any non-CCC analyte is greater than 15%, a new initial calibration should be performed.[33]

[33]Alternatively, rather than reattempting linear calibration, it may be appropriate to use a non-linear calibration model. The non-linear option should be reserved for appropriate circumstances, such as the need to achieve low detection limits. Non-linear calibration may not be used to compensate for detector saturation at higher concentrations or to avoid proper instrument maintenance. See SW-846, Method 8000B, Section 7.5, (3rd edition, December, 1996).

TABLE 23

Initial Calibration Criteria for SVOC Analysis αΩ

Analyte Type*	Compound	Minimum Mean RF	Maximum RSD
B/N **SPCC**	N-Nitroso-di-n-propylamine	0.050	15%
B/N **SPCC**	Hexachlorocyclopentadiene	0.050	15%
Acid **SPCC**	2,4-Dinitrophenol	0.050	15%
Acid **SPCC**	4-Nitrophenol	0.050	15%
B/N **CCC**	Acenaphthene	—	30%
B/N **CCC**	1,4-Dichlorobenzene	—	30%
B/N **CCC**	Hexachlorobutadiene	—	30%
B/N **CCC**	Diphenylamine	—	30%
B/N **CCC**	Di-n-octyl phthalate	—	30%
B/N **CCC**	Fluoranthene	—	30%
B/N **CCC**	Benzo(a)pyrene	—	30%
Acid **CCC**	4-Chloro-3-methylphenol	—	30%
Acid **CCC**	2,4-Dichlorophenol	—	30%
Acid **CCC**	2-Nitrophenol	—	30%
Acid **CCC**	Phenol	—	30%
Acid **CCC**	Pentachlorophenol	—	30%
Acid **CCC**	2,4,6-Trichlorophenol	—	30%
ALL OTHER BNA TARGET ANALYTES		—	15%

*B/N denotes base/neutral fraction compound.
Acid denotes acid fraction compound.
BNA denotes base, neutral, and acid compounds.

Additional Calibration Criteria Applicable to All BNA Compounds (Target and QC)	
RT Evaluation	Agreement within ± 0.06 relative retention time units for RTs of each target analyte among the 5 calibration standards.
GC Performance	Symmetrical peaks, minimum tailing, good resolution. **Anthracene and phenanthrene should be separated by baseline. Benz[a]anthracene and chrysene should be separated by a valley whose height is less than 25% of the average peak height of these two compounds.**
MS Sensitivity	99% (minimum) target compound peaks recognized and identified in appropriate retention time window

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3.4.3 Calibration Verification

The calibration relationship established during the initial calibration should be verified at periodic intervals. Calibration verification consists of three steps that should be performed at the beginning of each 12-hour analytical shift. A minimum of one calibration verification should be reported per sample set, even if the set is completed in fewer than twelve hours of analysis time.

The calibration verification steps include:

(1) DFTPP is analyzed and results compared to the criteria in the method (or *TABLE 22*) to verify mass calibration and tuning. The criteria must be met prior to further analysis.

(2) A calibration verification standard at a concentration near the midpoint of the calibration range is analyzed and assessed for the following criteria. The calibration standard should contain all target compounds, surrogates, and internal standards.

(1) System performance check. Each SPCC in the calibration verification standard must meet the minimum response factor listed in *TABLE 23*. If the minimum response factors are not met, the system must be evaluated and corrective action taken before beginning or continuing sample analysis.

(2) Calibration validation: The response factors for the CCCs in the calibration verification standard are compared to the mean response factors determined in the initial calibration through a percent difference (%D) calculation.[34] The %D is calculated as follows:

$$\frac{RF_V - \overline{RF}}{\overline{RF}} \; x \; 100$$

where: RF_V = the response factor for the verification standard, and
$\overline{RF}$ = the mean response factor from the initial calibration.

The %D criteria must meet the criteria in *TABLE 24* for the initial calibration to be considered valid. If the CCCs are not in or added to the list of target analytes for the project, the %D criteria should be applied to all analytes.

If the criteria in *TABLE 24* are not met for any one compound, then corrective action must be taken prior to the analysis of samples. If attempts to correct the problem are unsuccessful, a new initial five-point calibration must be performed.

[34] RF %D is calculated when the calibration model used is average response factor. If a non-linear regression fit model is used, percent drift is calculated instead. See SW-846 Method 8000B.

(C) Calibration Standard Internal Standard Check: Internal standards criteria for the calibration verification standard must be evaluated during or immediately after data acquisition. The retention time for any internal standard in the calibration verification standard must not change by more than 30 seconds from the RTs of the internal standards in the mid-range concentration standard of the most recent initial calibration sequence. The peak area counts for the internal standards in the calibration verification standard must change by less than a factor of 2 (-50% to +100%) from the area counts for the internal standard peaks in the mid-range concentration standard of the most recent initial calibration sequence.

If either of these criteria are not met, the mass spectrometer must be inspected for malfunctions, and corrections must be made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required. Corrections should be documented in the case narrative. Internal standard RT and area count data should be reported for both analyses (before and after corrective action).

TABLE 24

Response Factor %D Calibration Verification Criteria for SVOC Analysis αΩ

Analyte Type	Compound	Maximum %D
CCC	**All Semivolatile CCCs** (Base/Neutral and Acid)	20%
Alternatively, if CCCs are not in analyte list: **ALL TARGET ANALYTES**		20%

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If the criteria in *TABLE 24* are not met for any one required compound, then corrective action must be taken prior to the analysis of samples. If attempts to correct the problem are unsuccessful, a new initial five-point calibration should be performed.

3.4.4 Blanks

A method blank is an organic-free water sample taken through the entire preparatory and analytical procedure step by step, including all the reagents and solvents in the quantity required by the method. The organic-free water used must meet the specific method requirements. Prior to being subjected to the method procedure, interferents should not be observed in the water at the method detection limit of the compounds of interest.

(1) Frequency. One method blank should be extracted and analyzed with each group of samples analyzed on the same instrument during the same analytical shift. At a minimum, this frequency should be one method blank per 12-hour shift per instrument.

When the sample extracts are subjected to cleanup procedures, the associated method blank must also be subjected to the same cleanup procedures.

(2) Control Criteria. Analysis of a semivolatile method blank should meet the following criteria:

(A) The phthalate esters on the target analyte list (which are common laboratory contaminants in the analysis of semivolatile organic compounds) should be present at a concentration no greater than 5 times the estimated quantitation limit (EQL).

(B) Concentrations of target analytes observed in the method blank should be no higher than the highest of:

(i) The laboratory's MDL for the analyte;
(ii) 5% of the regulatory limit for that analyte (applicable only if the sample results will be compared to that regulatory limit); or
(iii) 5% of the measured concentration in the sample.

(3) Failure of control criteria. If any laboratory method blank exceeds these criteria, the laboratory should take corrective action. The source of the contamination should be located, the contaminant concentration should be reduced, and all relevant information should be documented. All samples processed with the contaminated method blank should be re-extracted/repurged and reanalyzed.

(4) Results and reporting. The laboratory should report results of all volatile method blank analyses. However, the laboratory should not subtract the results of the method blank from those of any associated samples.

3.4.5 Matrix Spike and Matrix Spike Duplicate (or Matrix Spike and Unspiked Duplicates)

To document the effect of the matrix, at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair (MS/MSD) should be analyzed. In matrix spike/matrix spike duplicate analysis, predetermined quantities of stock solutions of target analytes are added to a sample matrix prior to sample extraction and analysis. Samples are split into duplicates, spiked and analyzed. Percent recoveries are calculated for each of the analytes detected and used to assess bias due to sample matrix effects. The relative percent difference (RPD) between the split samples is calculated and used to assess analytical precision.

If the option to analyze a matrix spike and unspiked duplicates is chosen, the single matrix spike is used to assess bias, and the RPD of unspiked split samples is used to assess precision. However, if unspiked duplicates are used in place of the MSD, it may be difficult to assess the precision of target analytes present at low concentrations or below detection limits. Unspiked duplicates should only be used if samples are expected to contain target analytes at concentrations at least an order of magnitude higher than the detection limit. If samples are not expected to contain target analytes (or are expected to contain target analytes at concentrations near the detection limit), the laboratory should use a matrix spike and matrix spike duplicate pair.

(1) MATRIX SPIKE. The matrix spike analysis is designed to provide information about the effect of the sample matrix on the preparation and measurement methodology. The matrix spike (and MSD, if applicable) is a measure of the bias attributed to sample matrix effects, not just laboratory process effects on phase or concentration characteristics. The sample matrix includes the target and non-target analytes present in the sample or group of samples: naturally occurring compounds as well as contaminants. Therefore, the spiked sample must be from the same project as the case of field samples. **If the spiked sample is not from the same project as the field samples, matrix effects cannot be determined and sample results must be qualified as estimated.**

At least one MS should be performed on each group of samples of a similar matrix type from the same project (e.g., water, sludges, soil) for each group of 10 (or fewer) samples received per project. However, it is not necessary to spike samples when the concentration of the analyte in the unspiked sample exceeds 0.1%.

(A) Selection of sample to be spiked. For many projects, DQO requirements may dictate that the sampling team select the sample to be spiked based on a pre-site visit evaluation. The rationale for specifying a specific sample to be spiked should be documented by the facility. This does not preclude the laboratory from spiking a sample of its own selection in addition to those samples provided by the facility. **However, samples identified as field blanks may not be spiked.**

(B) Compounds to be spiked. Matrix spiking solutions should be prepared from semivolatile organic compounds which are representative of the compounds being investigated. It is highly recommended that the MS/MSD be prepared using all target analytes in order to accurately interpret matrix effects on sample results.

At a minimum, the matrix spike should include the following compounds:

Base/Neutrals	Acids
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3-methylphenol
N-Nitroso-di-n-propylamine	4-Nitrophenol
1,4-Dichlorobenzene	

If these compounds are not representative of the target analytes, additional compounds that are representative must be added. % Recoveries and RPDs (if applicable) should be reported for all analytes spiked.

The matrix spiking solutions should not be prepared from the same standards as the calibration standards. However, the same spiking standard prepared for the matrix spike may be used for the LCS.

(C) Spike concentrations. The concentration of the stock spiking solution and the final concentration of the spike in the sample will be specified in the individual methods of analysis and generally should be followed. However, the concentration may require adjustment to meet project DQOs. For example, if a method modification or a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute matrix spiking solutions may be required.

(D) Control limits. Recommended control limits for the MS (and MSD, if applicable) % Recovery are listed in *TABLE 25A*. The % Recovery for each component is calculated as follows. When the concentration of the spiked analyte is less than the detection limit in the unspiked sample, use SR = 0 for purposes of calculating % R:

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

Where: SSR = Spiked Sample Result
SR = Sample Result (prior to spiking)
SA = Spike Added

(2) MS/MSD OR UNSPIKED MATRIX DUPLICATE PAIR. At least one MSD or one unspiked duplicate should be performed on each group of samples of a similar matrix type from the same project (e.g., water, sludges, soil) for each group of 10 (or fewer) samples received per project. To assess precision, the Relative Percent Difference is defined by the following equation. MS/MSD and matrix duplicate RPDs should be reported. Recommended RPD control limits are listed in *TABLE 25A*.

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

Where: D_1 = %R Value for First Duplicate (unspiked sample or MS)
D_2 = %R Value for Second Duplicate (unspiked dup. or MSD)

3.4.6 Field Duplicate Sample Analysis

At least one field duplicate sample should be collected for every matrix sampled per sampling event. If large numbers of samples are collected, it is recommended that at least one field duplicate pair be collected for every 20 samples collected. Field duplicates should be treated as independent samples for preparation, analysis, and reporting purposes.

The RPD for each analyte detected should be calculated and reported in the QC report. The RPD is calculated in the same way for matrix duplicates and laboratory replicates as is indicated above for matrix spike duplicates. If the RPD exceeds the control limits listed in *TABLE 25B*, data should be qualified as estimated.

TABLE 25A

Recommended MS/MSD and Matrix Duplicate Control Criteria for SVOC Analysis αΩ

Matrix:	**Water**		**Other Matrices**	
Compound	**MS/MSD Spike % R**	**MS/MSD or Duplicate RPD**	**MS/MSD Spike % R**	**MS/MSD or Duplicate RPD**
Phenol	12-110	42	26-100	42
2-Chlorophenol	27-123	40	25-102	50
1,4-Dichlorobenzene	36-100	28	28-104	28
N-Nitroso-di-n-propylamine	41-116	38	41-126	38
1,2,4-Trichlorobenzene	39-100	28	38-107	28
4-Chloro-3-methylphenol	23-100	42	26-103	42
Acenaphthene	46-118	31	31-137	31
4-Nitrophenol	10-100	50	11-114	50
2,4-Dinitrotoluene	24-100	38	28-100	47
Pentachlorophenol	9-103	50	17-109	50
Pyrene	26-127	31	35-142	36
ALL OTHER B/N ANALYTES	25-125	35	25-140	40
ALL OTHER ACID ANALYTES	10-125	50	10-125	50

TABLE 25B

Recommended Control Limits for Field Duplicate Sample Analysis RPD αΩ

Compounds	**Aqueous Samples RPD**	**Soil, Sludge, Sediment, Oil, & Waste Samples RPD**
ALL TARGET ANALYTES	± 25 %	± 40 %

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

3.4.7 Analysis of Surrogates

The recommended surrogates for GC/MS analysis of SVOCs are phenol-d_6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d_5, 2-fluorobiphenyl, and p-terphenyl-d_{14}. Other compounds may be used as surrogates as necessary or appropriate to meet project objectives.

Every blank, standard, environmental sample (including matrix spike/matrix spike duplicate and matrix duplicate samples) should be spiked with surrogate compounds prior to extraction or processing.

Surrogates should be spiked into samples as directed in the appropriate extraction method. The concentration of the surrogate spiking solution and final concentration of surrogate in the sample extracts should be appropriate to the project DQOs. Surrogate concentrations in the sample extracts should generally either be near the middle of the calibration range or approximately ten times the quantitation limit of the surrogate. If a more sensitive mass spectrometer or method modification is used to achieve lower detection limits, a spiking solution more dilute than the usual 100-200 μg/mL may be required.

If the surrogate quantitation limit is unknown, the average quantitation limit of method target analytes may be used to estimate a surrogate quantitation limit. Determine the appropriate surrogate concentration for the blank extracts after all extraction, cleanup, and concentration steps.

(1) Control criteria for surrogates. Surrogate spike recoveries should not fall outside the control limits listed in the analytical method (if any) or developed by the laboratory. The control limits used should be specified in the project QAPP. Recommended control criteria for semivolatile surrogate recoveries are listed in *TABLE 26*.

Surrogate recoveries are calculated as:

$$\text{Recovery (\%)} = \frac{\text{Concentration (or amount) found}}{\text{Concentration (or amount) added}} \times 100$$

TABLE 26
Recommended Surrogate Spike Control Criteria for SVOC Analysis αΩ

Matrix:	**Water**	**Soil & Other Matrices**
Compound	**Surrogate Spike %Recovery**	**Surrogate Spike %Recovery**
Nitrobenzene-d_5	35-114	23-120
2-Fluorobiphenyl	43-116	30-115
Terphenyl-d_{14}	33-141	18-137
Phenol-d_6	10-110	24-113
2-Fluorophenol	21-110	25-121
2,4,6-Tribromophenol	10-123	19-122

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(2) Corrective action for surrogate recoveries. The laboratory should take corrective action if either of the following conditions exists during the analysis of environmental samples for semi-volatile parameters:

- Recovery of any one surrogate compound in either the base-neutral or the acid fraction is below 10%, or

- Recoveries of two surrogate compounds in either the base-neutral or the acid fraction are outside the surrogate spike recovery limits.

If either of these conditions occur, the laboratory should take the following corrective actions:

(A) Check calculations to ensure that there are no errors; check internal standard and surrogate spiking solutions for degradation, contamination, etc. Examine chromatograms for interfering peaks and integrated peak areas. Also check instrument performance.

(B) If the above steps fail to identify the problem, and if DQOs have not been met, then reanalyze the extract.

(C) If after reanalysis of the extract, surrogate recoveries still do not meet control criteria, and if DQOs have not been met, then re-extract and reanalyze the sample.

(D) If re-extraction and reanalysis of the sample does not solve the problem (i.e., surrogate recoveries are outside the requirements for both analyses), then submit the surrogate spike recovery data and the sample data from both analyses. Distinguish between the initial analysis and the reanalysis on all data deliverables. (See Section 3.5, Corrective Action for Organic Analysis by GC/MS, for additional information.)

(3) Dilution of surrogate response. Some samples may require dilution in order to bring one or more target analytes within the calibration range or to overcome significant interferences with some analytes. This may result in the dilution of the surrogate responses to the point that the recoveries can not be measured. If the surrogate recoveries are available from a less-diluted or undiluted aliquot of the sample or sample extract, those recoveries may be used to demonstrate that the surrogates were within the QC limits, and no further action is required. However, the results of both the diluted and undiluted (or less-diluted) analyses should be provided to the data user.

Although the surrogates may be diluted out of certain sample extracts, their retention times in the calibration standards may be useful in tracking retention time shifts. Whenever the observed retention time of a surrogate is outside of the established retention time window, the analyst is advised to determine the cause and correct the problem before continuing analyses.

3.4.8 Internal Standards

All samples (including matrix spike/matrix spike duplicate and matrix duplicate samples), standards, and blanks must be spiked with the internal standards.

(1) Choosing internal standards. The recommended internal standards are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}. Depending on the project target analytes, it may be appropriate to use other compounds as internal standards. Other compounds may be used as long as they permit most components of interest in a chromatogram to have retention times of 0.80 - 1.20 relative to one of the internal standards.

(2) Control criteria for internal standards. Area counts of the internal standard peaks in the samples (environmental and QC) must be within 50-200% of the area of the corresponding peak in the 12-hour calibration verification standard. The retention times for each internal standard in the sample must not vary by more than 30 seconds. If these criteria are not met, the analysis of all affected samples should be repeated.

(3) Assignment of internal standards for quantitation. The internal standard selected for quantitation of a particular target compound should be the internal standard that has a retention time closest to the retention time of the analyte being measured. *TABLE 28* lists the possible assignment of target compounds to the recommended internal standards for quantitation.

3.4.9 Laboratory Control Sample

A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the all the target analytes at the same concentrations as the matrix spike, and the % recoveries are calculated. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. LCS percent recoveries should be reported.

TABLE 27

Recommended Laboratory Control Sample %R Criteria for Organic Analysis αΩ

Matrix:	**Water**	**Soil & Other Matrices**
Compound	**LCS %Recovery**	**LCS %Recovery**
ALL TARGET ANALYTES	70-130	60-140

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

TABLE 28

Semivolatile Internal Standards with Corresponding Analytes Assigned for Quantitation [αΩ]

1,4-Dichlorobenzene-d_5	**Naphthalene-d_5**	**Acenaphthene-d_{10}**	**Phenanthrene-d_{10}**	**Chrysene-d_{12}**	**Perylene-d_{12}**
Aniline	Acetophenone	Acenaphthene	4-Aminobiphenyl	Benzidine	Benzo(b)fluoranthene
Benzyl alcohol	Benzoic acid	Acenaphthylene	Anthracene	Benzo(a)anthracene	Benzo(k)fluoranthene
Bis(2-chloroethyl)ether	Bis(2-chloroethoxy)methane	1-Chloronaphthalene	4-Bromophenyl phenyl	Bis(2-ethylhexyl)phthalate	Benzo(g,h,i)perylene
Bis(2-chloroisopropyl)ether	4-Chloroaniline	2-Chloronaphthalene	ether	Butyl benzyl phthalate	Benzo(a)pyrene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl	Di-n-butyl phthalate	Chrysene	Dibenz(a,j)acridine
1,2-Dichlorobenzene	2,4-Dichlorophenol	ether	4,6-Dinitro-2-methylphenol	3,3'-Dichlorobenzidine	Dibenz(a,h)anthracene
1,3-Dichlorobenzene	2,6-Dichlorophenol	Dibenzofuran	Diphenylamine	p-Dimethylaminoazobenzene	
1,4-Dichlorobenzene	α,α-	Diethyl phthalate	Fluoranthene	Pyrene	
Ethyl methanesulfonate	Dimethylphenethylamine	Dimethyl phthalate	Hexachlorobenzene	Terphenyl-d_{14} *(surr.)*	
2-Fluorophenol *(surr.)*	2,4-Dimethylphenol	2,4-Dinitrophenol	N-Nitrosodiphenylamine	7,12-Dimethylbenz[a]anthracene	
Hexachloroethane	Hexachlorobutadiene	2,4-Dinitrotoluene	Pentachlorophenol	Di-n-octyl phthalate	
Methyl methanesulfonate	Isophorone	2,6-Dinitrotoluene	Pentachloronitrobenzene	Indeno(1,2,3-cd)pyrene	
2-Methylphenol	2-Methylnaphthalene	Fluorene	Phenacetin	3-Methylcholanthrene	
4-Methylphenol	Naphthalene	2-Fluorobiphenyl *(surr.)*	Phenanthrene		
N-Nitrosodimethylamine	Nitrobenzene	Hexachlorocyclopentadiene	Pronamide		
N-Nitroso-di-n-propylamine	Nitrobenzene-d_8 *(surr.)*	1-Naphthylamine			
Phenol	2-Nitrophenol	2-Naphthylamine			
Phenol-d_6 *(surr.)*	N-Nitrosodi-n-butylamine	2-Nitroaniline			
2-Picoline	N-Nitrosopiperidine	3-Nitroaniline			
	1,2,4-Trichlorobenzene	4-Nitroaniline			
		4-Nitrophenol			
		Pentachlorobenzene			
		1,2,4,5-Tetrachlorobenzene			
		2,3,4,6-Tetrachlorophenol			
		2,4,6-Tribromophenol *(surr)*			
		2,4,5-Trichlorophenol			
		2,4,5-Trichlorophenol			

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3.5 Corrective Action for Organic Analysis by GC/MS

Whenever an analytical procedure is out-of-control (fails to meet control criteria), the problem must be found, corrected and the analysis repeated [35] (which may require re-extraction). The analytical procedure is out-of-control when any one or more of the following conditions occurs:

(1) **Whenever the *tuning results* do not meet control criteria: STOP! The instrument must be retuned and recalibrated before proceeding with analysis!** (See Section 3.3.1 (VOCs) and Section 3.4.1 (SVOCs) for details.)

(2) **Whenever the *initial calibration results* do not meet control criteria: STOP! The instrument must be recalibrated before proceeding with analysis!** (See Section 3.3.2.1 (VOCs) and Section 3.4.2.1 (SVOCs) for details.)

(3) **Whenever the *calibration verification results* (CCC and SPCC) do not meet control criteria: STOP! The instrument must be recalibrated before proceeding with analysis!** (See Section 3.3.3 (VOCs) and Section 3.4.3 (SVOCs) for details.)

(4) Whenever the method blank results exceed the detection limit. (See Section 3.3.4 (VOCs) and Section 3.4.4 (SVOCs) for details.)

(5) Whenever matrix spikes, surrogates, internal standards, or other laboratory fortified sample results fail to meet control criteria.[36] (See Sections 3.3.5, 3.3.7, and 3.3.9 (VOCs) and Sections 3.4.5, 3.4.7, and 3.4.9 (SVOCs) for details.)

(6) Whenever matrix spike duplicate or matrix duplicate results fall outside control limits. (See Section 3.3.5 (VOCs) and Section 3.4.5 (SVOCs) for details.); or

(7) Whenever the chromatographic performance or mass spec sensitivity is poor (e.g., rising baseline, peak broadening, tailing, poor resolution, etc.).

When the "out-of-control" conditions listed in items (3) through (7) above occur, re-extraction (if applicable) and reanalysis of all affected samples should be performed. It should be noted that for MS/MSD, matrix duplicate, and method blank failure, the affected samples would include all field samples prepared or purged with the out-of-control QC sample(s). Report the results from both analyses, distinguishing between the initial analysis and reanalysis on all data deliverables.[37]

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[35] Whenever a quality control sample indicates a biased high result (e.g., high matrix spike recovery) and the sample results are all below detection limit for all target compounds, then reanalysis is not required. However, the laboratory should make every effort to correct the problem for future analysis. The RPD requirement must be met on the matrix spike duplicate even if matrix spike is biased high.

[36] The corrective action for internal standards does not require re-extraction of samples affected by out-of-control results. However, reanalysis of the affected sample is required. (See Section 3.4.8, Internal Standards).

[37] IDEM's position on holding times for reanalysis of out-of-control results is that it would be preferred that sample analysis be performed within holding times, but if that is not possible, reanalysis, based on analytical requirements, may still need to be performed for analytical obligations to be considered met. The acceptance of results analyzed beyond holding time requirements will be predicated on DQO and threshold requirements along

If QC results from the re-extraction and reanalysis are also outside the acceptance limits, but the analysis of a laboratory control sample demonstrates that the method is in control, then the problem is related to sample matrix and analytical requirements will be considered met. (See SW-846 Method 8000B, Section 8.5.5.) If re-extraction and reanalysis of the sample does not solve the problem and the laboratory control sample results are also outside of acceptance limits, instrument maintenance may be required. Major maintenance such as cleaning an ion source, cleaning quadrupole rods, etc. require returning to the initial calibration step.

3.6 Analysis of Semivolatile Organic Compounds by Gas Chromatography with Electron Capture Detector (GC/ECD)

GC/ECD analysis is most familiar in the environmental field as the technique of choice for quantitative analysis of organochlorine pesticides and polychlorinated biphenyl compounds (PCBs). GC/ECD may also be used to analyze other types of SVOCs such as halogenated hydrocarbons and chlorinated herbicides. Although IDEM prefers the use of GC/ECD for pesticides and PCBs, they may be analyzed by gas chromatography using other detector types, such as electrolytic conductivity detectors (ELCD). If a non-ECD detector is used, then follow the method and manufacturer's recommendations. The principles in this section can be used as guidance for non-ECD instruments.

3.6.1 General Requirements and Considerations

(1) Extraction and cleanup: Samples must be extracted prior to analysis. Based on sample matrix characteristics, follow criteria in appropriate extraction techniques. Most samples will require cleanup of extracts before determinative analysis to remove phthalate esters, sulfur, and other non-target interferents.

(2) Holding times and preservatives: Preservative techniques specified in **Table 1 - ORGANICS** or **Table 1 Supplemental** should be followed based on sample characteristics. Holding time requirements for both samples and extracts should be adhered to.

(3) Compound identification: Compound identification based on single-column analysis should be confirmed on a second column, or should be supported by at least one other qualitative technique. GC/MS may be used as qualitative confirmation *if sensitivity permits (I.e.,* GC/MS may be used if the detected compound is present in high enough concentration to be detectable by standard GC/MS, or if a more sensitive GC/MS system or method modification is utilized to achieve low enough detection limits.)

(4) Multicomponent analytes: When samples contain more than one target analyte that is a multicomponent mixture (e.g., Chlordane, Aroclors), a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of multicomponent analytes that have been subjected to environmental degradation

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with analyst's best judgement. Resampling may be required in some cases. If reanalysis is performed past the holding time, both analysis results must be reported.

("weathering") or degradation by treatment technologies. Such weathered multicomponent mixtures may have significant differences in peak patterns than those of standards.

3.6.2 Initial Calibration

An external standard calibration procedure is preferred for analysis of pesticides and Aroclors because of the sensitivity of the electron capture detector.[38] Surrogates and, if applicable, internal standards should be present in the calibration standards at the same concentration as the sample extracts.

3.6.2.1 CALIBRATION STANDARDS

(1) Single-component analytes (including individual PCB congeners): Calibration standards for single-component analytes may be prepared separately for each analyte or as an analyte mixture. If there are a large number of target analytes (e.g., the full analyte list for SW-846 Method 8081A), and standard mixtures are used, it is recommended that the target analytes be divided between two separate calibration mixtures.[39] This will minimize potential resolution and quantitation problems and allow determination of DDT and Endrin breakdown.

For each surrogate and analyte of interest, prepare calibration standards at a minimum of five concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with an appropriate solvent. One of the external standards should be at a concentration near, but above, the method detection limit, and one should be at or near the midrange of the curve. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector. For each analyte, at least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project, which may include establishing compliance with a regulatory or action limit.

(2) Chlordane, Toxaphene, and similar multi-component analytes (other than Aroclors): Separate external calibration standards are required for each multi-component target analyte. Standard mixtures should not be used.[40]

Once the linear range has been established for the instrument and column for which the analysis is being performed, a single-point calibration may be used for multi-component analytes (unless a three-point or five-point calibration is necessary to meet the DQOs for a specific project). [41] A single calibration standard near the mid-point of the expected calibration range of each multi-component analyte is included with the initial calibration of the single component analytes for pattern recognition, so that the analyst is familiar with the patterns and retention times on each column.

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[38]Exception: Internal standard calibration is recommended when PCBs are to be determined as individual congeners.

[39]The two standard mixture approach is also consistent with the CLP SOW's Analytical Method for Pesticides/Aroclors use of "Individual Standard Mixtures A and B."

[40]The exception to this is Aroclors 1016 and 1260. See Section 3.6.2.1(3), Aroclors, below.

[41]This does not apply to Aroclors. See Section 3.6.2.1(3), Aroclors, below.

(3) Aroclors

(A) When all seven Aroclors are target analytes as part of a standard analyte list: A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five Aroclor mixtures (i.e., 1221, 1232, 1242, 1248, and 1254). As a result, a multi-point initial calibration employing a mixture of Aroclors 1016 and 1260 at five concentrations should be sufficient to demonstrate the linearity of the detector response without the necessity of performing initial calibrations for each of the seven Aroclors.

Such a mixture can be used as a standard to demonstrate that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample. However, this standard cannot be used to identify or quantitate Aroclors other than 1016 or 1260.

Prepare a minimum of five calibration standards containing equal concentrations of both Aroclor 1016 and Aroclor 1260 by dilution of the stock standard with an appropriate solvent. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector.

Single standards of each of the other five Aroclors are required to aid the analyst in pattern recognition. Assuming that the Aroclor 1016/1260 standards described above have been used to demonstrate the linearity of the detector, these single standards of the remaining five Aroclors can also be used to determine the calibration factor for each Aroclor. Prepare a standard for each of the other Aroclors. The concentrations should correspond to the mid-point of the linear range of the detector.

(A) When specific site-related Aroclors are target analytes: In situations where only a few Aroclors are of interest for a specific project, a five-point initial calibration of each site-related Aroclor should be run. In this case, the 1016/1260 mixture and the pattern recognition standards described in section 3.6.2.1(3)(A), above, need not be run. Prepare the standards as indicated in section 3.6.2.1(1).

3.6.2.2 CALIBRATION PROCESS (EXTERNAL STANDARD PROCEDURE)[42]

Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph (e.g., 1-3 µL injections). Tabulate peak height or area responses against the mass injected. In the case of multi-component analytes, a minimum of 3 peaks (and preferably 5 peaks) should be chosen for each multi-component analyte and responses for each of these peaks tabulated. The results are used to prepare a calibration curve or to calculate a calibration factor (CF) for each

[42]If an internal standard calibration procedure is used (e.g., for PCB congeners) peak responses are tabulated against concentrations rather than mass. A response factor is calculated instead of a calibration factor. See Section 3.3.2 and SW-846 Method 8000B for the RF calculation and linearity determination.

analyte. The CF is defined as the ratio of the detector response to the amount (mass) injected. It can be calculated for each analyte at each standard concentration as follows:

$$CF = \frac{\text{Total Peak Area of the Compound in the Standard *}}{\text{Mass of the Compound injected (in nanograms)}}$$

*For multi-component pesticides and Aroclors, a separate CF is calculated for for each characteristic peak in the mixture. Each multicomponent analyte will have 3-5 CFs for each concentration calibration standard.

3.6.2.3 INITIAL CALIBRATION CONTROL CRITERIA

The mean and standard deviation of the calibration factors across the five concentrations for each analyte are calculated; from these the relative standard deviation for each analyte is calculated:

$$\text{RSD} = \frac{\text{SD}}{\overline{\text{CF}}} \; x \; 100$$

If the relative standard deviation (RSD) of the calibration factor ≤20% over the working range, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve. If linearity through the origin cannot be assumed (i.e., the criteria in Table 28 cannot met), the analysis should be stopped and the problem found and corrected before analysis of samples can begin. A calibration curve may need to be used instead of the mean calibration factor. (See SW-846 Method 8000B, December 1996.)[43]

TABLE 28
Initial Calibration CF RSD Criteria for GC Analysis αΩ

Compound	RSD for Standard CFs across all concentrations
EACH TARGET ANALYTE	≤ 20 %

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

[43]SW-846 Method 8000B, Section 7.5, (3rd edition Final Update III, December 1996) provides criteria for linear as well as for non-linear calibration models. A linear calibration curve is preferred. In some situations it may be appropriate to use a non-linear calibration model. The non-linear option should be reserved for appropriate circumstances, such as the need to achieve low detection limits. Non-linear calibration may not be used to compensate for detector saturation at higher concentrations or to avoid proper instrument maintenance.

A new calibration curve (or calibration factor), should be prepared whenever a new column or detector is installed. The initial calibration data, calibration factors, and RSDs calculated should be reported with the analysis results.

3.6.3 Establishment of Retention Time Windows

Retention time windows are crucial to the identification of target compounds. Absolute retention times are used for compound identification.[44] Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loadings and normal chromatographic variability. The width of the retention time window should be carefully established to minimize the occurrence of both false positive and false negative results. Retention time windows that are too narrow may result in false negatives or may cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified. Overly wide retention time windows may result in false positive results that cannot be confirmed upon further analysis.

IDEM recommends the following approach to establishing retention time windows. Other approaches may be used, but must be documented by the analyst and should be summarized in the case narrative. The recommended approach is:

(1) Before establishing windows, make sure the GC system is within optimum operating conditions. Make three injections of all single component standard mixtures and multi-component analytes (such as PCBs) over the course of a 72-hour period. Serial injections over a period of less than 72 hours may result in retention time windows that are too tight (narrow).

(2) Record the retention time for each single component analyte and surrogate to three decimal places (e.g., 0.007). (Recording retention times to three decimal places rather than only two should minimize the instances in which the standard deviation is calculated as zero.)

(3) Calculate the mean and standard deviation of the three absolute retention times for each single component analyte and surrogate. For multi-component analytes, choose three to five major peaks and calculate the mean and standard deviation for each of those peaks.

(4) If the standard deviation of the retention times for a target compound is 0.000 (i.e., no difference between the absolute retention times), then the laboratory may either collect data from additional injections of standards or use a default standard deviation of 0.01 minutes.

(5) The width of the retention time window for each analyte, surrogate, and major constituent in multi-component analytes is defined as ± 3 times the standard deviation of the mean absolute retention time established during the 72-hour period. If the default standard deviation in paragraph (4), above, is employed, the width of the window will be 0.03 minutes.

(6) Establish the center of the retention time window for each analyte and surrogate by using the absolute retention time for each analyte and surrogate from the calibration verification

[44]When PCBs are determined as congeners by an internal standard technique, absolute retention times may be used in conjunction with relative retention times (relative to the internal standard).

standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.

(7) The laboratory should calculate absolute retention time windows for each analyte and surrogate on each GC column and instrument. New retention time windows should be established ~~and~~ whenever a new GC column is installed. The retention time windows should be reported with the analysis results in support of the identifications made.

3.6.4 Calibration Verification

The calibration relationship established during the initial calibration should be verified by injecting a calibration verification standard at periodic intervals:

(1) At the beginning of each 12-hour analytical shift, prior to conducting sample analyses. Analysts should alternate the use of high and low concentration mixtures of single-component analytes and multi-component analytes for calibration verification.

(2) A calibration verification standard should also be injected at intervals of, at a minimum, once every 20 samples and at the end of the analysis sequence. It is recommended that an interval of once every 10 samples be used (to minimize the number of samples requiring re-injection when QC limits are exceeded).

3.6.4.1 CALIBRATION VERIFICATION CONTROL CRITERIA should include the following:

(A) The calibration factor for each analyte should not exceed a ± 15 percent difference from the mean calibration factor calculated for the initial calibration. The percent difference is calculated as:

$$\%\,Difference = \frac{CF_v - \overline{CF_i}}{\overline{CF_i}}\,x\,100$$

where: CF_v = the calibration factor from the analysis of the calibration verification standard, and

$\overline{CF_i}$ = the mean calibration factor calculated for the initial calibration

(B) The retention time for each analyte in the calibration verification standard must fall within the retention time window established with the midlevel concentration standard during the initial calibration.

If the criteria in Table 29 are not met for any analyte, then corrective action must be taken prior to continuing analysis of samples. If attempts to correct the problem are unsuccessful, a new initial calibration must be performed. All samples analyzed after the last calibration verification standard that met the control criteria should be reanalyzed.

The laboratory should report the results from the calibration verifications.

TABLE 29

Calibration Verification Control Criteria for GC Analysis[αΩ]

Compound	Calibration Factor % D	Retention Time
ALL TARGET ANALYTES	85-115	In Window (established with initial calibration midlevel standard RT)

Additional Calibration Criteria Applicable to All Compounds (Target and QC)	
GC Performance	Symmetrical peaks, minimum tailing, good resolution

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

3.6.5 Degradation

DDT and endrin are easily degraded in the injection port. Breakdown occurs when the injection port liner is contaminated with buildup of high boiling residue from sample injection or when the injector contains metal fittings. Check for degradation problems by injecting a standard containing only 4,4'-DDT and Endrin. Presence of the degradation products of 4,4′-DDT (4,4'-DDE and 4,4'-DDD) and Endrin (Endrin ketone or Endrin aldehyde) indicates breakdown. If degradation of either DDT or Endrin exceeds 15%, take corrective action before proceeding further with calibration. Calculate percent breakdown as follows:

$$\% \text{ Breakdown of DDT} = \frac{\text{Sum of degradation peak areas (DDD + DDE)}}{\text{Sum of all peak areas (DDT + DDD + DDT)}} \times 100$$

$$\% \text{ Breakdown of Endrin} = \frac{\text{Sum of degradation peak areas (aldehyde + ketone)}}{\text{Sum of all peak areas (Endrin + aldehyde + ketone)}} \times 100$$

The breakdown of DDT and Endrin should be measured before samples are analyzed and at the beginning of each 12-hour analytical shift. Injector maintenance and recalibration should be completed if the breakdown is exceeds the criteria in Table 30 for either compound. The laboratory should report the results from the degradation/ breakdown calculations.

TABLE 30

Degradation Control Criteria for GC Analysis of Pesticides αΩ

Compound	% Breakdown Criteria
4,4'-DDT	≤ 15%
Endrin	≤ 15%

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

3.6.6 Blanks

Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. A method blank is an organic-free water sample carried through all stages of the sample preparation and measurement steps. The organic-free water used must meet the specific method requirements. Prior to being subjected to the method procedure, interferents should not be observed in the water at the method detection limit of the compounds of interest.

(1) Frequency. One method blank should be extracted and analyzed with each group of samples analyzed on the same instrument during the same analytical shift. At a minimum, this frequency should be one method blank per 12-hour shift per instrument. When the sample extracts are subjected to cleanup procedures, the associated method blank must also be subjected to the same cleanup procedures. Method blanks may be run immediately after the calibration verification analyses to confirm that laboratory contamination does not cause false positive results.

(2) Control Criteria. Analysis of a method blank for analysis of pesticides, PCBs, and other semivolatile organic compounds by GC/ECD should meet the following criteria:

(A) Interferences by phthalate esters introduced during sample preparation can cause a major problem in analysis of pesticides, PCBs, and other semivolatile organic compounds. The phthalate esters on the target analyte list should be present at a concentration no greater than 5 times the estimated quantitation limit (EQL).

(B) Concentrations of target analytes observed in the method blank should be no higher than the highest of:

(i) The laboratory's MDL for the analyte;
(ii) 5% of the regulatory limit for that analyte (applicable only if the sample results will be compared to that regulatory limit); or
(iii) 5% of the measured concentration in the sample.

(3) Failure of control criteria. If any laboratory method blank indicates contamination (concentration of any target analyte detected in the blank exceeds the above control criteria), then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples.

If method blank contamination cannot be attributable to carryover, the laboratory should take corrective action. The source of the contamination should be located, reduced, and documented. All samples processed with the contaminated method blank should be re-extracted and reanalyzed.

(4) Results and reporting. The laboratory should report results of all method blank analyses. However, the laboratory should not subtract the results of the method blank from those of any associated samples.

Method blanks and/or solvent blanks may also be used to check for contamination by carryover from a high-concentration sample or standard into subsequent samples. Whenever an unusually concentrated sample is encountered, it should be followed by injection of a solvent blank to check for cross contamination. If there is evidence that carryover may have occurred, then the samples should be reanalyzed.

3.6.7 Matrix Spike/Matrix Spike Duplicates (or Matrix Spike and Unspiked Duplicates)

To document the effect of the matrix, at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair (MS/MSD) should be analyzed. In matrix spike/matrix spike duplicate analysis (MS/MSD), predetermined quantities of stock solutions of ~~all~~ target analytes are added to a sample matrix prior to sample extraction/digestion and analysis. Samples are split into duplicates, spiked and analyzed. Percent recoveries are calculated for each of the analytes detected and used to assess bias due to sample matrix effects. The relative percent difference (RPD) between the split samples is calculated and used to assess analytical precision. The concentration of the spike should be at the regulatory standard level (if TCLP is being run) or the estimated or actual method quantitation limit.

If the option to analyze a matrix spike and unspiked duplicates is chosen, the single matrix spike is used to assess bias, and the RPD of unspiked split samples is used to assess precision. However, if unspiked duplicates are used in place of the MSD, it may be difficult to assess the precision of target analytes present at low concentrations or below detection limits. Unspiked duplicates should only be used if samples are expected to contain target analytes at concentrations at least an order of magnitude higher than the detection limit. If samples are not expected to contain target analytes (or are expected to contain target analytes at concentrations near the detection limit), the laboratory should use a matrix spike and matrix spike duplicate pair.

(1) MATRIX SPIKE. The matrix spike analysis is designed to provide information about the effect of the sample matrix on the preparation and measurement methodology. The matrix spike (and MSD, if applicable) is a measure of the bias attributed to sample matrix effects, not just laboratory process effects on phase or concentration characteristics. The sample matrix includes the target and non-target analytes present in the sample or group of samples: naturally occurring compounds as well as contaminants.

Therefore, the spiked sample must be from the same project as the case of field samples. *If the spiked sample is not from the same project as the field samples, matrix effects cannot be determined and sample results must be qualified as estimated*. **Samples identified as field blanks may not be spiked.**

At least one MS should be performed on each group of samples of a similar matrix type from the same project (e.g., water, sludges, soil) for each group of 20 (or fewer) samples received per project. However, it is not necessary to spike samples when the concentration of the analyte in the unspiked sample exceeds 0.1%.

(A) Compounds to be spiked . Matrix spiking solutions should be prepared from compounds which are representative of the compounds being investigated. It is recommended that the MS/MSD be prepared using all single-component target analytes in order to accurately interpret matrix effects on sample results.

(i) Pesticides analysis: At a minimum, the matrix spike should contain -BHC (Lindane), Heptachlor, Aldrin, Dieldrin, Endrin, and 4,4'-DDT.

(ii) PCBs Analysis: When samples are known or expected to contain specific Aroclors or PCB congeners, the target Aroclors or congeners should be spiked. If samples are not expected to contain target analytes, the Aroclor 1016/1260 mixture (or, at a minimum Aroclor 1260) should be spiked.

The matrix spiking solutions should not be prepared from the same standards as the calibration standards. However, the same spiking standard prepared for the matrix spike may be used for the LCS.

(B) Spike concentrations. The concentrations of the spiked compounds in the samples should be at or below the regulatory limit, health-protective action level, or 1 to 5 times higher than the background concentration, whichever concentration would be greater.

(C) Control limits. Recommended control limits for the MS (and MSD, if applicable) minimum spiked compounds' % Recovery are listed in Table 31. The % Recovery for each component is calculated as follows. When the concentration of the spiked analyte is less than the detection limit in the unspiked sample, use SR = 0 for purposes of calculating % R:

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

Where: SSR = Spiked Sample Result
SR = Sample Result (prior to spiking)
SA = Spike Added

(2) MS/MSD OR UNSPIKED MATRIX DUPLICATE PAIR. At least one MSD or one unspiked duplicate should be performed on each group of samples of a similar matrix type from the same project (e.g., water, sludges, soil) for each group of 10 (or fewer) samples received

per project. To assess precision, the Relative Percent Difference is defined by the following equation. MS/MSD and matrix duplicate RPDs should be reported. Recommended RPD control limits are listed in Table 31.

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \; x\; 100$$

Where: D_1 = %R Value for First Duplicate (unspiked sample or MS)
D_2 = %R Value for Second Duplicate (unspiked dup. or MSD)

TABLE 31
Recommended MS/MSD and Matrix Duplicate Control Criteria for GC/ECD Analysis αΩ

Matrix:	**Water**		**Other Matrices**	
Compound	**MS/MSD Spike % Recovery**	**MS/MSD or Duplicate RPD**	**MS/MSD Spike % Recovery**	**MS/MSD or Duplicate RPD**
-BHC (Lindane)	56-123	**15**	46-127	50
Heptachlor	40-131	20	35-130	31
Aldrin	40-120	22	34-132	43
Dieldrin	52-126	**18**	31-134	38
Endrin	56-121	21	42-139	45
4,4'-DDT	38-127	27	23-134	50
Aroclor 1016/1260	56-103	20	40-140	50
ALL OTHER ANALYTES	40-130	30	30-140	50

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

3.6.8 Field Duplicate Sample Analysis

At least one field duplicate sample should be collected for every matrix sampled per sampling event. If large numbers of samples are collected, it is recommended that at least one field duplicate pair be collected for every 20 samples collected. Field duplicates should be treated as independent samples for preparation, analysis, and reporting purposes.

The RPD for each analyte detected should be calculated and reported in the QC report. The RPD is calculated in the same way for matrix duplicates and laboratory replicates as is indicated

above for matrix spike duplicates. If the RPD exceeds the control limits listed in *TABLE 32*, data should be qualified as estimated.

TABLE 32
Recommended Control Limits for GC/ECD Field Duplicate Sample Analysis RPD αΩ

Compounds	Aqueous Samples RPD	Soil, Sludge, Sediment, Oil, & Waste Samples RPD
ALL TARGET ANALYTES	± 30 %	± 50 %

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

3.6.9 Surrogate Standards

The performance of the method should be monitored using surrogate compounds. Surrogate standards should be added to all samples, method blanks, matrix spikes, and calibration standards. The following compounds are recommended as possible surrogates:

(1) Pesticides analysis: Decachlorobiphenyl (DCB) and tetrachloro-m-xylene (TCMX) have been found to be a useful pair of surrogates for both single-column and dual-column instrument configurations. However, if the chromatographic conditions of a dual-column configuration cannot be adjusted to preclude co-elution of a target analyte with either DCB or TCMX, another compound such as 4-Chloro-3-nitrobenzotrifluoride may be used.

(2) PCBs as Aroclors: The recommended surrogate is decachlorobiphenyl. Tetrachloro-m-xylene may be used in addition to DCB.

(3) PCB congeners: When PCB congeners are to be determined, decachlorobiphenyl is recommended for use as an internal standard and cannot also be used as a surrogate. The use of tetrachloro-m-xylene is recommended.

Surrogate recoveries should not exceed the control limits listed in the analytical method or developed by the laboratory. Proceed with corrective action when % Recovery for either surrogate is outside of the control limits. Recommended control limits are listed in Table 33. Surrogate recoveries are calculated as follows:

$$\text{Recovery (\%)} = \frac{\text{Concentration (or amount) found}}{\text{Concentration (or amount) added}} \times 100$$

TABLE 33
Recommended Control Limits for GC/ECD Surrogate % Recovery [αΩ]

Compounds	Aqueous Samples % Recovery	Soil, Sludge, Sediment, Oil, & Waste Samples % Recovery
Decachlorobiphenyl	30-150	30-150
Tetrachloro-m-xylene	30-150	30-150
4-Chloro-3-nitrobenzotrifluoride, other	30-150	30-150

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

3.6.10 Internal Standards

The use of an internal standard is highly recommended when individual PCB congeners are to be determined. The use of an internal standard when pesticides or Aroclors are to be determined is optional, but can be beneficial, especially when low concentrations are being analyzed. Compounds to use as internal standards are recommended in the analytical methods. Recommended internal standards for certain analyte types are listed below:

(1) PCB congeners: The recommended internal standard is decachlorobiphenyl. It is added to each sample extract and calibration standard prior to analysis.

(2) Aroclors: An internal standard is not usually used when PCBs are determined as Aroclors.

(3) Organochlorine pesticides: 1-Bromo-2-nitrobenzene is suggested as an internal standard for dual-column analysis and can also be used for single-column analysis. Pentachloronitrobenzene is recommended for single-column analysis when it is not a target analyte.

(4) Control criteria for internal standards. Whenever quantitation is accomplished using an internal standard, internal standard data must be evaluated for acceptance. The measured area of the internal standard must be no more than 50% different from the average area calculated during calibration. All samples for which the internal standard peak area falls outside the control limits must be reanalyzed.

3.6.11 Confirmation of Target Analyte Identification

Tentative identification of single-component analyte occurs when a peak from a sample extract falls within the established retention time window for a specific target analyte. Identification of multi-component analytes is based on retention time windows established for three to five

major peaks (i.e., components of the mixture). Each positive tentative analysis should be confirmed in one of the following ways. The confirmation results should be reported:

(1) Confirmation on a second GC column of dissimilar stationary phase:

(A) Single-column analysis: When confirmation is made on a second column, the second analysis should meet all the QC criteria described, just as is required for the primary analysis. In order to be used for confirmation, retention time windows must have been established for the second GC column. In addition, the analyst must demonstrate the sensitivity of the second column analysis. This demonstration must include the analysis of a standard of the target analyte at a concentration at least as low as the concentration estimated from the primary analysis.

(B) Dual-column analysis: When simultaneous analyses are performed from a single injection (using a dual column/dual detector system with columns of different polarities), identification and confirmation are incorporated in a single run. In this case, it is not practical to designate one column as the analytical (primary) column and the other as the confirmation column. Since the calibration standards are analyzed on both columns, the results for both columns must meet the calibration acceptance criteria. If the retention times of the peaks on both columns fall within the retention time windows on the respective columns, target analyte identification has been confirmed.

(2) Confirmation by GC/MS analysis. GC/MS confirmation may be used in conjunction with either single- or dual-column analysis if the concentration is sufficient for detection by GC/MS. Full-scan GC/MS will normally require a concentration of approximately 10 ng/μL in the final extract for each target analyte. Ion trap or selected ion monitoring (SIM) will normally require a concentration of approximately 1 ng/μL. The following requirements apply to confirmation by GC/MS:

(A) The GC/MS must be calibrated for the specific target analytes being confirmed.

(B) GC/MS may not be used for confirmation when concentrations are below 1 ng/μL in the extract.

(C) GC/MS confirmation should be accomplished by analyzing the same extract that is used for GC/ECD analysis and the extract of the associated blank from the GC/ECD analysis.

(D) A QC reference sample containing the compound must also be analyzed by GC/MS. The concentration of the QC reference sample must demonstrate that the target analytes identified by GC/ECD can be confirmed by GC/MS.

3.6.12 Laboratory Control Sample

A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same target analytes at the same concentrations as the matrix spike, and the % recoveries are calculated. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. LCS percent recoveries should be reported.

TABLE 34
Recommended Laboratory Control Sample %R Criteria for Organic Analysis αΩ

Matrix:	**Water**	**Soil & Other Matrices**
Compound	**LCS %Recovery**	**LCS %Recovery**
ALL TARGET ANALYTES	70-130	60-140

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

3.6.13 Corrective Action for Organic Analysis by GC/ECD

Whenever an analytical procedure is out-of-control (fails to meet control criteria), the problem must be found, corrected and the analysis repeated.[45] The analytical procedure is out-of-control when any one or more of the following conditions occurs:

(1) **Whenever the *initial calibration results* do not meet control criteria: STOP! The instrument must be recalibrated before proceeding with analysis! (**See Section 3.6.2.3 for details.)

(2) **Whenever the *calibration verification results* do not meet control criteria: STOP! The instrument must be recalibrated before proceeding with analysis!** (See Section 3.6.4.1 for details.)

[45]Whenever a quality control sample indicates a biased high result (e.g., high matrix spike recovery) and the sample results are all below detection limit for all target compounds, then reanalysis is not required. However, the laboratory should make every effort to correct the problem for future analysis. The RPD requirement must be met on the matrix spike duplicate even if matrix spike is biased high.

(3) Whenever the method blank results exceed the control criteria. (See section 3.6.6 for details.)

(4) Whenever matrix spikes, surrogates, internal standards, laboratory control samples or other laboratory fortified sample results fall outside control limits. (See Sections 3.6.7, 3.6.9, 3.6.10, and 3.6.12 for details.)

(5) Whenever matrix spike duplicate or matrix duplicate results fall outside control limits. (See Section 3.6.7 for details.)

(6) Whenever the chromatographic performance is poor (e.g., rising baseline, peak broadening, tailing, poor resolution, etc.); or

(7) Degradation of DDT or Endrin is outside control limits. (See Section 3.6.5 for details.)

When the "out-of-control" conditions listed in items (3) through (7) above occur, re-extraction and reanalysis of all affected samples should be performed. It should be noted that for MS/MSD, matrix duplicate, and blank failure the affected samples would include all field samples prepared with the out-of-control QC sample(s). Report the results from both analyses, distinguishing between the initial analysis and reanalysis on all data deliverables.[46]

If QC results from the re-extraction and reanalysis are also outside the acceptance limits but the analysis of a laboratory control sample demonstrates that the method is in control, then the problem is related to sample matrix and analytical requirements will be considered met. (See SW-846, Method 8000B, Section 8.5.5.) If re-extraction and reanalysis of the sample does not solve the problem and the laboratory control sample results are also outside of acceptance limits, instrument maintenance may be required. Major maintenance (such as changing a column) requires returning to the initial calibration step.

3.7 Analysis of Semivolatile and Non Volatile Organic Compounds by High Performance Liquid Chromatography (HPLC)

HPLC can be used for analysis of many semivolatile, nonvolatile, and some volatile organic compounds. For environmental applications it can be especially useful for analysis of polynuclear aromatic hydrocarbons (PAHs) and other compounds for which human health and ecological risk-based protective levels are lower than can be achieved by standard full scan GC/MS. This section will focus on analysis of PAHs for use in risk assessment. Guidance in this section refers to HPLC

[46]Reanalysis of out-of-control samples may require that the reanalysis be performed past holding time requirements. IDEM's position on holding times for reanalysis of out-of-control results is that it would be preferred that sample analysis be done within holding times, but if that is not possible, reanalysis, based on analytical requirements, may still need to be performed for analytical obligations to be considered achieved. If reanalysis is performed past the holding time, both analysis results must be reported. The acceptance of results for samples analyzed beyond holding time requirements will be predicated on DQO and threshold requirements. Resampling may be required in some cases.

using non-MS detection: specifically, fluorescence and/or UV detectors. HPLC/MS techniques utilize different criteria than presented here. Refer to the analytical method for guidance.

3.7.1 General Requirements and Considerations

(1) Extraction and cleanup: Samples must be extracted prior to analysis. Based on sample matrix characteristics, follow criteria in appropriate extraction techniques. To achieve maximum sensitivity, the extract must be concentrated to 1 mL. If interferences prevent proper detection of the analytes of interest, extracts may undergo silica gel column cleanup prior to analysis. Additional cleanup steps may be required by some samples.

(2) Interference considerations: The sensitivity of the HPLC technique usually depends on the level of interferences rather than instrumental limitations. When interferences are present, the level of sensitivity will be lower. Non-target PAHs present in the sample matrix may pose significant interference problems.

(3) Holding times and preservatives: Preservative techniques specified in Table 1 - ORGANICS or Table 1 Supplemental should be followed based on sample characteristics. Holding time requirements for both samples and sample extracts should be adhered to.

(4) Detection: It is recommended that a combination of fluorescence and UV detectors are used. UV detection is applicable to a wide range of analytes and is less sensitive to RT fluctuation than fluorescence. However, UV does not provide sufficient sensitivity to quantitate some PAHs at sub-ppb concentrations, and hence to meet risk-based health protective levels, particularly for carcinogens. Fluorescence provides improved sensitivity, but not all target compounds fluoresce (e.g., acenaphthylene). A UV detector or a UV-Visible diode array detector (DAD) coupled to a fluorescence detector maximizes both sensitivity and selectivity. For compounds that fluoresce and for which UV detection can provide sufficient sensitivity, obtaining spectra from both detectors provides the additional advantage of combining identification and confirmation of target analytes in a single analysis.

(5) Confirmation of compound identification: Compound identification by HPLC using non-MS detection should be supported by at least one additional qualitative technique unless the composition of the sample matrix has been well established by prior analyses.

3.7.2 Initial Calibration

Initial calibration must be performed and documented for each instrument used to analyze samples. HPLC calibration may be accomplished through either an internal or external standard calibration procedure. However, it may be difficult to find compounds for use as internal standards that can be chromatographically resolved from the target analytes.

Initial calibration should be performed using a minimum of 5 concentrations. The concentration range of the calibration standards should bracket the concentrations of target compounds expected to be seen in the field samples and should be wide enough to meet the project DQOs. At least one standard should be at a concentration near, but above, the MDL. If data will be compared to risk-based human health or ecological protective levels, this low standard concentration for each analyte must be as low or lower than the risk-based level to

which sample concentrations will be compared. The remaining standards should correspond to the range of concentrations found in typical samples or should define the working range of the HPLC system.

3.7.2.1 EXTERNAL STANDARD CALIBRATION PROCEDURE: Prepare calibration standards at a minimum of five concentration levels for each analyte by dilution of stock standards with an appropriate solvent. Inject each calibration standard into the instrument using the same technique that will be used to introduce the actual samples (e.g. 5-100 μL injections). Tabulate peak area or height responses against the mass of analyte injected. The results can be used to prepare a calibration curve for each compound.

Alternatively, the ratio of detector response to mass of analyte injected, defined as the calibration factor (CF), can be calculated for each analyte at each standard concentration. If the CF is a constant over the working range (the relative standard deviation (RSD) is $\leq$20%), linearity through the origin can be assumed and the average calibration factor can be used in place of a calibration curve to determine sample concentrations. The CF is calculated as follows:

$$CF = \frac{\text{Total Peak Area of the Compound in the Standard}}{\text{Mass of the Compound injected (in nanograms)}}$$

3.7.2.2 INTERNAL STANDARD CALIBRATION PROCEDURE: If an internal standard calibration procedure is used, a known constant amount of one or more internal standards is added to each calibration standard and each sample prior to analysis. Compounds selected for use as internal standards should be similar in analytical behavior to the compounds of interest, but should not be expected to be present in the samples. The analyst must demonstrate that the measurement of the internal standards is not affected by method or matrix interferences and that the internal standard can be chromatographically resolved from the target compounds.

Possible choices for internal standards might include brominated, fluorinated, or stable isotopically labeled PAH analogs. 4,4'-difluorobiphenyl is a possible internal standard candidate for early eluting compounds determined by UV adsorbance. A different compound would need to be chosen for the higher molecular weight, fluorescent analytes.

Prepare calibration standards at a minimum of five concentration levels for each analyte by adding volumes of one or more stock standard solutions to a volumetric flask. To each calibration standard add a known amount of one or more internal standards, and dilute to volume with an appropriate solvent. Inject each calibration standard into the instrument using the same technique that will be used to introduce the actual samples (e.g. 5-100 μL injections). Tabulate peak area or height responses against the concentration for each compound and internal standard. Calculate the response factor for each compound at each concentration. If the RF value is constant over the working range (the RSD is $\leq$20%), linearity through the origin can be assumed and the average RF can be used to calculate sample concentrations. The RF is calculated using the following equation:

$$RF = \frac{A_s - C_{is}}{A_{is} - C_s}$$

where: A_s = Peak area of the analyte or surrogate
A_{is} = Peak area of the internal standard
C_s = Concentration of the analyte or surrogate
C_{is} = Concentration of the internal standard

3.7.2.3 INITIAL CALIBRATION CONTROL CRITERIA: Calculate the RSD for each analyte across all concentrations using the mean and standard deviation of the CFs or RFs :

$$RSD = \frac{SD}{\overline{CF}} \times 100 \qquad \text{or} \qquad RSD = \frac{SD}{\overline{RF}} \times 100$$

The RSD criteria in Table 35 must be met for linearity through the origin to be assumed using the CF or RF approach. If linearity through the origin cannot be assumed, the analysis should be stopped and the problem found and corrected before analysis of samples can begin. A calibration curve may need to be used instead of the mean CF for the external calibration procedure or the mean RF for the internal standard procedure. (See SW-846 Method 8000B, December 1996.)[47]
A new calibration curve (or calibration factor or response factor) should be prepared whenever a new column or detector is installed. The initial calibration data (and curve if used), calibration or response factors, and RSDs should be reported with the analysis results.

TABLE 35
Initial Calibration RSD Criteria for Assumption of Linearity in HPLC Analysis αΩ

Compound	External Calibration	Internal Calibration
	RSD for **Calibration Factors** across all concentrations	**RSD** for **Response Factors** across all concentrations
EACH TARGET	≤ 20 %	≤ 20 %

αΩ Environmental laboratory numerical reports are results of analytical processes, including field episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

3.7.3 Establishment of Retention Time Windows

[47]SW-846 Method 8000B, Section 7.5, (3rd edition Final Update III, December 1996) provides criteria for linear as well as for non-linear calibration models. Linear calibration curves are preferred. At times, it may be appropriate to use a non-linear calibration model. The non-linear option should be reserved for appropriate circumstances, such as the need to achieve low detection limits. Non-linear calibration may not be used to compensate for detector saturation at higher concentrations or to avoid proper instrument maintenance.

Retention time windows are crucial to the identification of target compounds. Absolute retention times are used for compound identification when external standard calibration procedures are used. When an internal standard technique is used, absolute retention times may be used in conjunction with relative retention times (relative to the internal standard).

Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loadings and normal chromatographic variability. The width of the retention time window should be carefully determined to minimize the occurrence of both false positive and false negative results. Retention time windows that are too narrow may result in false negatives or may cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified. Overly wide retention time windows may result in false positive results that cannot be confirmed upon further analysis.

IDEM recommends the following approach to establishing retention time windows when an external standard calibration procedure is used. Other approaches may be used, but must be documented by the analyst and should be summarized in the case narrative. The recommended approach is:

(1) Before establishing windows, make sure the HPLC system is within optimum operating conditions. Make three injections of all standards (or standard mixtures) over the course of a 72-hour period. Serial injections over a period of less than 72 hours may result in retention time windows that are too tight (narrow).

(2) Record the retention time for each analyte and surrogate to three decimal places (e.g., 0.007). (Recording retention times to three decimal places rather than only two should minimize the instances in which the standard deviation is calculated as zero.)

(3) Calculate the mean and standard deviation of the three absolute retention times for each analyte and surrogate.

(4) If the standard deviation of the retention times for a target compound is 0.000 (i.e., no difference between the absolute retention times), then the laboratory may either collect data from additional injections of standards or use a default standard deviation of 0.01 minutes.

(5) The width of the retention time window for each analyte and surrogate is defined as ± 3 times the standard deviation of the mean absolute retention time established during the 72-hour period. If the default standard deviation in paragraph (4), above, is employed, the width of the window will be 0.03 minutes.

(6) Establish the center of the retention time window for each analyte and surrogate by using the absolute retention time for each analyte and surrogate from the calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.

(7) The laboratory should calculate absolute retention time windows for each analyte and surrogate on each HPLC column and instrument. New retention time windows should be established whenever a new HPLC column is installed. The retention time windows should be reported with the analysis results in support of the identifications made.

3.7.4 Calibration Verification

The calibration relationship established during the initial calibration should be verified at periodic intervals:

(1) A calibration verification must be injected at the beginning of each 12-hour analytical shift, prior to conducting sample analyses.

(2) If external standard calibration procedures are used, the midpoint calibration verification standard should also be injected at intervals during the 12-hour analytical shift. It is recommended that an interval of once every 10 samples be used (to minimize the number of samples requiring re-injection when QC limits are exceeded).

3.7.4.1 CALIBRATION VERIFICATION CONTROL CRITERIA should include the following:

(A) Response criteria:[48] If an external standard calibration technique is used, the calibration factor for each analyte should not exceed a ± 15 percent difference from the mean calibration factor calculated for the initial calibration. If an internal standard calibration technique is used, the response factor for each analyte should not exceed a ± 15 percent difference from the mean response factor calculated for the initial calibration The percent difference is calculated as:

$$\%\,Difference = \frac{CF_v - \overline{CF_i}}{\overline{CF_i}}\,x\,100 \quad \textbf{or} \quad \%\,Difference = \frac{RF_v - \overline{RF_i}}{\overline{RF_i}}$$

where: CF_v and RF_v are the calibration factor and response factor (whichever applies) from the analysis of the calibration verification standard;

and $\overline{CF_i}$ and $\overline{RF_i}$ are the mean calibration factor and the mean response factor from the initial calibration.

(B) The retention time for each analyte in the calibration verification standard must fall within the retention time window established with the midlevel concentration standard during the initial calibration.

If the criteria in *TABLE 36* are not met for any analyte during calibration verification, then corrective action must be taken prior to continuing with analysis of samples. If attempts to correct the response %Difference problem are unsuccessful, a new initial calibration must be performed. If attempts to correct the retention time window problem are unsuccessful, new RT windows must be determined. All samples analyzed after the last calibration verification standard that met the control criteria should be reanalyzed. The laboratory should report the results from the calibration verifications.

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[48] If a calibration curve is used rather than CF or RF, % Drift should be calculated instead of % Difference. Acceptance criteria for % Drift are 85-115%. % Drift is calculated as:

$$\%Drift = \frac{Calculated\ concentration - Theoretical\ concentration}{Theoretical\ concentration}$$

TABLE 36

Calibration Verification Control Criteria for HPLC Analysis[αΩ]

Compound	Calibration Factor % D or Response Factor % D	Retention Time
ALL TARGET ANALYTES	85-115	In Window (established with initial calibration midlevel standard RT)
Additional Calibration Criteria Applicable to All Compounds (Target and QC)		
GC Performance	Symmetrical peaks, minimum tailing, good resolution	

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

3.7.5 Blanks

Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. A method blank is an organic-free water sample carried through all stages of the sample preparation and measurement steps. The organic-free water used must meet the specific method requirements. Prior to being subjected to the method procedure, interferents should not be observed in the water at the method detection limit of the compounds of interest.

(1) Frequency. Method blanks should be prepared at a frequency of at least 5%. That is, at least one method blank should be extracted and analyzed with each group of up to 20 samples analyzed on the same instrument during the same analytical shift. When the sample extracts are subjected to cleanup procedures, the associated method blank must also be subjected to the same cleanup procedures. Method blanks may be run immediately after the calibration verification analyses to confirm that laboratory contamination does not cause false positive results.

(2) Control Criteria. Concentrations of target analytes observed in the method blank should be no higher than the highest of:

(i) The laboratory's MDL for the analyte;
(ii) 5% of the regulatory limit for that analyte (applicable only if the sample results will be compared to that regulatory limit); or
(iii) 5% of the measured concentration in the sample.

(3) Failure of control criteria. If any laboratory method blank indicates contamination (concentration of any target analyte detected in the blank exceeds the above control

criteria), then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples.

If method blank contamination cannot be attributable to carryover, the laboratory should take corrective action. The source of the contamination should be located, reduced, and documented. All samples processed with the contaminated method blank should be re-extracted and reanalyzed.

(4) Results and reporting. The laboratory should report results of all method blank analyses. However, the laboratory should not subtract the results of the method blank from those of any associated samples.

Method blanks and/or solvent blanks may also be used to check for contamination by carryover from a high-concentration sample or standard into subsequent samples. Whenever an unusually concentrated sample is encountered, it should be followed by injection of a solvent blank to check for cross contamination. If there is evidence that carryover may have occurred, then the samples should be reanalyzed.

3.7.6 Matrix Spike/Matrix Spike Duplicates (or Matrix Spike and Unspiked Duplicates)

To document the effect of the matrix, at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair (MS/MSD) should be analyzed. In matrix spike/matrix spike duplicate analysis, predetermined quantities of stock solutions of target analytes are added to a sample matrix prior to sample extraction/digestion and analysis. Samples are split into duplicates, spiked and analyzed. Percent recoveries are calculated for each of the analytes detected and used to assess bias due to sample matrix effects. The relative percent difference (RPD) between the split samples is calculated and used to assess analytical precision. The concentration of the spike should be at the estimated or actual method quantitation limit.

If the option to analyze a matrix spike and unspiked duplicates is chosen, the single matrix spike is used to assess bias, and the RPD of unspiked split samples is used to assess precision. However, if unspiked duplicates are used in place of the MSD, it may be difficult to assess the precision of target analytes present at low concentrations or below detection limits. Unspiked duplicates should only be used if samples are expected to contain target analytes at concentrations at least an order of magnitude higher than the detection limit. If samples are not expected to contain target analytes (or are expected to contain target analytes at concentrations near the detection limit), the laboratory should use a matrix spike and matrix spike duplicate pair.

(1) MATRIX SPIKE. The matrix spike analysis is designed to provide information about the effect of the sample matrix on the preparation and measurement methodology. The matrix spike (and MSD, if applicable) is a measure of the bias attributed to sample matrix effects, not just laboratory process effects on phase or concentration characteristics. The sample matrix includes the target and non-target analytes present in the sample or group of samples: naturally occurring compounds as well as contaminants. Therefore, the spiked sample must be from the same project as the case of field samples. *If the spiked sample is not from the same project as the field samples, matrix effects cannot be determined and sample results must be qualified as estimated.* **Samples identified as field blanks may not be spiked.**

At least one MS should be performed on each group of samples of a similar matrix type from the same project (e.g., water, sludges, soil) for each group of 20 (or fewer) samples received per project. However, it is not necessary to spike samples when the concentration of the analyte in the unspiked sample exceeds 0.1%.

(A) Compounds to be spiked . Matrix spiking solutions should be prepared from compounds which are representative of the compounds being investigated. It is recommended that the MS/MSD be prepared using all target analytes in order to accurately interpret matrix effects on sample results. The matrix piking solutions should not be prepared from the same standards as the calibration standards. However, the same spiking standard prepared for the matrix spike may be used for the LCS.

(B) Spike concentrations. The concentrations of the spiked compounds in the samples should be at or below the health-protective action level, or 1 to 5 times higher than the background concentration, whichever concentration would be greater.

(C) Calculations and Control limits. The laboratory should develop its own in-house acceptance criteria for spike recoveries. Recommended control limits for the MS (and MSD, if applicable) minimum spiked compounds' % Recovery are listed in Table 37. The % Recovery for each component is calculated as follows. When the concentration of the spiked analyte is less than the detection limit in the unspiked sample, use SR = 0 for purposes of calculating % R:

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

Where: SSR = Spiked Sample Result
SR = Sample Result (prior to spiking)
SA = Spike Added

(2) MS/MSD OR UNSPIKED MATRIX DUPLICATE PAIR. At least one MSD or one unspiked duplicate should be performed on each group of samples of a similar matrix type from the same project (e.g., water, sludges, soil) for each group of 10 (or fewer) samples received per project. To assess precision, the Relative Percent Difference is defined by the following equation. MS/MSD and matrix duplicate RPDs should be reported. The laboratory should develop its own in-house acceptance criteria for duplicate RPD. Recommended RPD control limits are listed in Table 37. The RPD is calculated as:

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

Where: D_1 = %R Value for First Duplicate (unspiked sample or MS)
D_2 = %R Value for Second Duplicate (unspiked dup. or MSD)

TABLE 37

Recommended MS/MSD and Matrix Duplicate Control Criteria for GC/ECD Analysis [αΩ]

Matrix:	Water		Other Matrices	
Compound	**MS/MSD Spike % Recovery**	**MS/MSD or Duplicate RPD**	**MS/MSD Spike % Recovery**	**MS/MSD or Duplicate RPD**
ALL TARGET ANALYTES	70-130	20	60-140	40

3.7.7 Field Duplicate Sample Analysis

At least one field duplicate sample should be collected for every matrix sampled per sampling event. If large numbers of samples are collected, it is recommended that at least one field duplicate pair be collected for every 20 samples collected. Field duplicates should be treated as independent samples for preparation, analysis, and reporting purposes.

The RPD for each analyte detected should be calculated and reported in the QC report. The RPD is calculated in the same way for matrix duplicates and laboratory replicates as is indicated above for matrix spike duplicates. If the RPD exceeds the control limits listed in *TABLE 38*, data should be qualified as estimated.

TABLE 38
Recommended Control Limits for HPLC Field Duplicate Sample Analysis RPD

Compounds	Aqueous Samples RPD	Soil, Sludge, Sediment, Oil, & Waste Samples RPD
ALL TARGET ANALYTES	± 30 %	± 50 %

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3.7.8 Surrogate Standards

The performance of the method should be monitored using at least one surrogate compound. The surrogate standards should be added to all samples, method blanks, matrix spikes, and calibration standards. Decafluorobiphenyl is recommended for use as the surrogate compound for PAH analysis. Additional PAH compounds may be used as surrogates provided that they are not expected to be present in the sample. Deuterated analogs of target analytes should not be used as surrogates for HPLC analysis due to coelution problems.

Surrogate recoveries should not exceed the control limits listed in the analytical method or developed by the laboratory. Proceed with corrective action when the % Recovery for any surrogate does not meet control limits. Recommended control limits are listed in Table 39. Surrogate recoveries are calculated as follows:

$$\text{Recovery (\%)} = \frac{\text{Concentration (or amount) found}}{\text{Concentration (or amount) added}} \times 100$$

TABLE 39

Recommended Control Limits for Surrogate % Recovery in HPLC Analysis of PAHs

Compounds	Aqueous Samples % Recovery	Soil, Sludge, Sediment, Oil, & Waste Samples % Recovery
Decachlorobiphenyl	30-150	30-150
other compounds	30-150	30-150

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

3.7.9 Control Criteria for Internal Standards (if internal standard calibration is performed)

Whenever quantitation is accomplished using an internal standard, internal standard data must be evaluated for acceptance. The measured area of the internal standard must be no more than 50% different from the average area calculated during calibration. All samples for which the internal standard peak area falls outside the control limits must be reanalyzed.

3.7.10 Confirmation of Target Analyte Identification

Tentative identification of single-component analyte occurs when a peak from a sample extract falls within the established retention time window for a specific target analyte. Compound identification by HPLC using non-MS detection should be supported by at least one additional qualitative technique. Some possible methods for confirmation of positive tentative analysis include:

(1) HPLC data from two different detectors (e.g., UV and fluorescence),

(2) HPLC/UV data at two different wavelengths, or

(3) Analysis on a second column with a dissimilar stationary phase.

Use of UV-Visible diode array detection may provide confirmation data from a single analysis provided that the laboratory can demonstrate this ability for typical sample extracts (not just standards) by comparison to another recognized confirmation technique.

Standard GC/MS techniques (e.g., SW-846 Method 8270C, unmodified) are not recommended for confirmation of carcinogenic PAHs due to insufficient sensitivity to achieve detection limits below risk-based human health and ecological protective levels. However, standard GC/MS is acceptable if concentrations of preliminarily identified target analytes are sufficiently high (e.g., > 660 μg/kg in solid matrices).

When confirmation is made by a second analysis, that analysis should meet all of the QC criteria required for the first analysis. The confirmation results should be reported.

3.7.11 Laboratory Control Sample

A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same target analytes at the same concentrations as the matrix spike, and the % recoveries are calculated. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. LCS percent recoveries should be reported.

TABLE 40

Recommended Laboratory Control Sample %R Criteria for Organic Analysis αΩ

Matrix:	**Water**	**Soil & Other Matrices**
Compound	**LCS %Recovery**	**LCS %Recovery**
ALL TARGET ANALYTES	70-130	60-140

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

3.7.12 Corrective Action for Organic Analysis by HPLC

Whenever an analytical procedure is out-of-control (fails to meet control criteria), the problem must be found, corrected, and the analysis repeated.[49] The analytical procedure is out-of-control when any one or more of the following conditions occurs:

[49]Whenever a quality control sample indicates a biased high result (e.g., high matrix spike recovery) and the sample results are all below detection limit for all target compounds, then reanalysis is not required. However, the laboratory should make every effort to correct the problem for future analysis. The RPD requirement must be met on the matrix spike duplicate even if matrix spike is biased high.

(1) **Whenever the *initial calibration results* do not meet control criteria: STOP! The instrument must be recalibrated before proceeding with analysis! (**See section 3.7.2.3 for details.)

(2) **Whenever the *calibration verification results* do not meet control criteria: STOP! The instrument must be recalibrated before proceeding with analysis!** (See section 3.7.4.1 for details.)

(3) Whenever the method blank results exceed the control criteria. (See section 3.7.5 for details.)

(4) Whenever matrix spikes, surrogates, internal standards, laboratory control samples or other laboratory fortified sample results fall outside control limits. (See sections 3.7.6, 3.7.8, 3.7.9, and 3.7.11 for details.)

(5) Whenever matrix spike duplicate or matrix duplicate results fall outside control limits. (See section 3.7.6 for details.)

(6) Whenever the chromatographic performance is poor (e.g., rising baseline, peak broadening, tailing, poor resolution, etc.); or

When the "out-of-control" conditions listed in items (3) through (6) above occur, re-extraction and reanalysis of all affected samples should be performed. It should be noted that for MS/MSD, matrix duplicate, and blank failure the affected samples would include all field samples prepared with the out-of-control QC sample(s). Report the results from both analyses, distinguishing between the initial analysis and reanalysis on all data deliverables.[50]

If QC results from the re-extraction and reanalysis ~~is~~ are also outside the acceptance limits but the analysis of a laboratory control sample demonstrates that the method is in control, then the problem is related to sample matrix and analytical requirements will be considered met. (See SW-846, Method 8000B, Section 8.5.5.) If re-extraction and reanalysis of the sample does not solve the problem and the laboratory control sample results are also outside of acceptance limits, instrument maintenance may be required. Major maintenance (such as changing a column) requires returning to the initial calibration step.

[50]Reanalysis of out-of-control samples may require that the reanalysis be performed past holding time requirements. IDEM's position on holding times for reanalysis of out-of-control results is that it would be preferred that sample analysis be done within holding times, but if that is not possible, reanalysis, based on analytical requirements, may still need to be performed for analytical obligations to be considered achieved. If reanalysis is performed past the holding time, both analysis results must be reported. The acceptance of results for samples analyzed beyond holding time requirements will be predicated on DQO and threshold requirements. Resampling may be required in some cases.

Epilogue[αΩ]

Section V provides guidance describing requirements for obtaining and documenting analytical data. The guidance set forth in this chapter is based on the analytical methods as specified in *Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods*, SW-846, Third Edition, Final Update III (SW-846, December 1996). It also draws from EPA methodology and guidance in *Methods for the Determination of Organic Compounds in Drinking Water, Supplement III* (EPA/600/R-95/131, August 1995) and *USEPA Contract Laboratory Program Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration*, OLM03.0, Revision OLM03.1 (August 1994). A working knowledge of SW-846 and the basic understanding of analytical process are requirements for the understanding of this chapter. The principles set forth in this chapter are adaptable to aid in the quality control and quality assurance of other applicable methods. Since it is not practical to prepare a guidance for every analytical method or technique, this document focuses on the most common. The analytical techniques focused on in this chapter are atomic absorption (flame and furnace), inductively coupled plasma emission spectroscopy, inductively coupled plasma emission spectroscopy/mass spectrometry (limited discussion), gas chromatography/mass spectrometry, gas chromatography/electron capture detector, high performance liquid chromatography (reverse phase), and limited wet chemistry techniques.

Analytical results and data quality interpretation, inferences or extrapolations, are dependent upon sample variances, aliquot variances, matrix variances, instrument variances, and method variances, etc. In many if not most cases, the analyst will be required to use professional judgement. Therefore, the tables provided are to be used with caution to determine if data quality has been affected or what corrective action steps may be necessary.

αΩ Environmental laboratory numerical reports are results of analytical processes, including field sampling episodes, based on a series of events requiring qualifications. Please refer to the chemistry analyst regarding pertinent data qualifications.

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APPENDIX I

SW-846 METHODS 7000A* and 8000B*

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METHOD 7000A
ATOMIC ABSORPTION METHODS

1.0 SCOPE AND APPLICATION

1.1 Metals in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in drinking, surface, and saline waters and domestic and industrial wastes. While drinking water free of particulate matter may be analyzed directly, ground water, other aqueous samples, EP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes require digestion prior to analysis for both total and acid leachable metals. Analysis for dissolved elements does not require digestion if the sample has been filtered and acidified.

1.2 Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and models of atomic absorption spectrophotometers. The data shown in Table 1 provide some indication of the detection limits obtainable by direct aspiration and by furnace techniques. For clean aqueous samples, the detection limits shown in the table by direct aspiration may be extended downward with scale expansion and upward by using a less sensitive wavelength or by rotating the burner head. Detection limits by direct aspiration may also be extended through concentration of the sample and/or through solvent extraction techniques. For certain samples, lower concentrations may also be determined using the furnace techniques. The detection limits given in Table 1 are somewhat dependent on equipment (such as the type of spectrophotometer and furnace accessory, the energy source, the degree of electrical expansion of the output signal), and are greatly dependent on sample matrix. Detection limits should be established, empirically, for each matrix type analyzed. When using furnace techniques, however, the analyst should be cautioned as to possible chemical reactions occurring at elevated temperatures which may result in either suppression or enhancement of the analysis element. To ensure valid data with furnace techniques, the analyst must examine each matrix for interference effects (see Step 3.2.1) and, if detected, treat them accordingly, using either successive dilution, matrix modification, or method of standard additions (see Step 8.7).

1.3 Where direct-aspiration atomic absorption techniques do not provide adequate sensitivity, reference is made to specialized procedures (in addition to the furnace procedure) such as the gaseous-hydride method for arsenic and selenium and the cold-vapor technique for mercury.

2.0 SUMMARY OF METHOD

2.1 Although methods have been reported for the analysis of solids by atomic absorption spectroscopy, the technique generally is limited to metals in solution or solubilized through some form of sample processing.

2.2 Preliminary treatment of waste water, ground water, EP extracts, and industrial waste is always necessary because of the complexity and variability of sample matrix. Solids, slurries, and

[51] *Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods*, SW-846, Third Edition**,** Final Update I (July 1992), Method 7000A, pp. 1-14. (Reprinted in its entirety from CD-ROM.)

suspended material must be subjected to a solubilization process before analysis. This process may vary because of the metals to be determined and the nature of the sample being analyzed. Solubilization and digestion procedures are presented in Step 3.2 (Sample Preparation Methods).

2.3 In direct-aspiration atomic absorption spectroscopy, a sample is aspirated and atomized in a flame. A light beam from a hollow cathode lamp or an electrodeless discharge lamp is directed through the flame into a monochromator, and onto a detector that measures the amount of absorbed light. Absorption depends upon the presence of free unexcited ground-state atoms in the flame. Because the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy.

2.4 When using the furnace technique in conjunction with an atomic absorption spectrophotometer, a representative aliquot of a sample is placed in the graphite tube in the furnace, evaporated to dryness, charred, and atomized. As a greater percentage of available analyte atoms is vaporized and dissociated for absorption in the tube rather than the flame, the use of smaller sample volumes or detection of lower concentrations of elements is possible. The principle is essentially the same as with direct aspiration atomic absorption, except that a furnace, rather than a flame, is used to atomize the sample. Radiation from a given excited element is passed through the vapor containing ground-state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground-state element in the vapor. The metal atoms to be measured are placed in the beam of radiation by increasing the temperature of the furnace, thereby causing the injected specimen to be volatilized. A monochromator isolates the characteristic radiation from the hollow cathode lamp or electrodeless discharge lamp, and a photosensitive device measures the attenuated transmitted radiation.

3.0 INTERFERENCES

3.1 Direct aspiration

3.1.1 The most troublesome type of interference in atomic absorption spectrophotometry is usually termed "chemical" and is caused by lack of absorption of atoms bound in molecular combination in the flame. This phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule, as in the case of phosphate interference with magnesium, or when the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame. The addition of lanthanum will overcome phosphate interference in magnesium, calcium, and barium determinations. Similarly, silica interference in the determination of manganese can be eliminated by the addition of calcium.

3.1.2 Chemical interferences may also be eliminated by separating the metal from the interfering material. Although complexing agents are employed primarily to increase the sensitivity of the analysis, they may also be used to eliminate or reduce interferences.

3.1.3 The presence of high dissolved solids in the sample may result in an interference from nonatomic absorbance such as light scattering. If background correction is not available, a nonabsorbing wavelength should be checked. Preferably, samples containing high solids should be extracted.

3.1.4 Ionization interferences occur when the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom, giving a positively charged ion. This type of interference can generally be controlled by the addition, to both standard and sample solutions, of a large excess (1,000 mg/L) of an easily ionized element such as K, Na, Li or Cs.

3.1.5 Spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. Interference can also occur when resonant energy from another element in a multielement lamp, or from a metal impurity in the lamp cathode, falls within the bandpass of the slit setting when that other metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

3.1.6 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

3.1.7 All metals are not equally stable in the digestate, especially if it contains only nitric acid, not nitric acid and hydrochloric acid. The digestate should be analyzed as soon as possible, with preference given to Sn, Sb, Mo, Ba, and Ag.

3.2 Furnace procedure

3.2.1 Although the problem of oxide formation is greatly reduced with furnace procedures because atomization occurs in an inert atmosphere, the technique is still subject to chemical interferences. The composition of the sample matrix can have a major effect on the analysis. It is those effects which must be determined and taken into consideration in the analysis of each different matrix encountered. To help verify the absence of matrix or chemical interference, the serial dilution technique (see Step 8.6) may be used. Those samples which indicate the presence of interference should be treated in one or more of the following ways:

1. Successively dilute and reanalyze the samples to eliminate interferences.

2. Modify the sample matrix either to remove interferences or to stabilize the analyte. Examples are the addition of ammonium nitrate to remove alkali chlorides and the addition of ammonium phosphate to retain cadmium. The mixing of hydrogen with the inert purge gas has also been used to suppress chemical interference. The hydrogen acts as a reducing agent and aids in molecular dissociation.

3. Analyze the sample by method of standard additions while noticing the precautions and limitations of its use (see Step 8.7.2).

3.2.2 Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. When this occurs, use either background correction or choose an alternate wavelength. Background correction may also compensate for nonspecific broad-band absorption interference.

3.2.3 Continuum background correction cannot correct for all types of background

interference. When the background interference cannot be compensated for, chemically remove the analyte or use an alternate form of background correction, e.g., Zeeman background correction.

3.2.4 Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the presence of air. Care must be taken, however, to prevent loss of the analyte.

3.2.5 Samples containing large amounts of organic materials should be oxidized by conventional acid digestion before being placed in the furnace. In this way, broad-band absorption will be minimized.

3.2.6 Anion interference studies in the graphite furnace indicate that, under conditions other than isothermal, the nitrate anion is preferred. Therefore, nitric acid is preferable for any digestion or solubilization step. If another acid in addition to nitric acid is required, a minimum amount should be used. This applies particularly to hydrochloric and, to a lesser extent, to sulfuric and phosphoric acids.

3.2.7 Carbide formation resulting from the chemical environment of the furnace has been observed. Molybdenum may be cited as an example. When carbides form, the metal is released very slowly from the resulting metal carbide as atomization continues. Molybdenum may require 30 seconds or more atomization time before the signal returns to baseline levels. Carbide formation is greatly reduced and the sensitivity increased with the use of pyrolytically coated graphite. Elements that readily form carbides are noted with the symbol (p) in Table 1.

3.2.8 For comments on spectral interference, see Step 3.1.5.

3.2.9 Cross-contamination and contamination of the sample can be major sources of error because of the extreme sensitivities achieved with the furnace. The sample preparation work area should be kept scrupulously clean. All glassware should be cleaned as directed in Step 4.8. Pipet tips are a frequent source of contamination. If suspected, they should be acid soaked with 1:5 nitric acid and rinsed thoroughly with tap and reagent water. The use of a better grade of pipet tip can greatly reduce this problem. Special attention should be given to reagent blanks in both analysis and in the correction of analytical results. Lastly, pyrolytic graphite, because of the production process and handling, can become contaminated. As many as five to ten high-temperature burns may be required to clean the tube before use.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer - Single- or dual-channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a graphical display.

4.2 Burner - The burner recommended by the particular instrument manufacturer should be used. For certain elements the nitrous oxide burner is required.

4.3 Hollow cathode lamps - Single-element lamps are preferred but multielement lamps may

be used. Electrodeless discharge lamps may also be used when available. Other types of lamps meeting the performance criteria of this method may be used.

4.4 Graphite furnace - Any furnace device capable of reaching the specified temperatures is satisfactory.

4.5 Graphical display and recorder - A recorder is recommended for furnace work so that there will be a permanent record and that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, peak shape, etc., can be easily recognized.

4.6 Pipets - Microliter, with disposable tips. Sizes can range from 5 to 100 uL as required. Pipet tips should be checked as a possible source of contamination prior to their use. The accuracy of automatic pipets must be verified daily. Class A pipets can be used for the measurement of volumes larger than 1 mL.

4.7 Pressure-reducing valves - The supplies of fuel and oxidant should be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.

4.8 Glassware - All glassware, polypropylene, or Teflon containers, including sample bottles, flasks and pipets, should be washed in the following sequence: detergent, tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water, and reagent water. (Chromic acid should not be used as a cleaning agent for glassware if chromium is to be included in the analytical scheme.) If it can be documented through an active analytical quality control program using spiked samples and reagent blanks that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. All reagents should be analyzed to provide proof that all constituents are below the MDLs.

5.2 Reagent water. All references to water in this method refer to reagent water unless otherwise specified. Reagent grade water will be of at least 16 Mega Ohm quality.

5.3 Nitric acid (concentrated), HNO_3. Use a spectrograde acid certified for AA use. Prepare a 1:1 dilution with water by adding the concentrated acid to an equal volume of water. If the reagent blank is less than the IDL, the acid may be used.

5.4 Hydrochloric acid (1:1), HCl. Use a spectrograde acid certified for AA use. Prepare a 1:1 dilution with water by adding the concentrated acid to an equal volume of water. If the reagent blank is less than the IDL, the acid may be used.

5.5 Fuel and oxidant - High purity acetylene is generally acceptable. Air may be supplied from a compressed air line, a laboratory compressor, or a cylinder of compressed air and should be clean and dry. Nitrous oxide is also required for certain determinations. Standard, commercially available argon and nitrogen are required for furnace work.

5.6 Stock standard metal solutions - Stock standard solutions are prepared from high purity metals, oxides, or nonhygroscopic salts using water and redistilled nitric or hydrochloric acids. (See individual methods for specific instructions.) Sulfuric or phosphoric acids should be avoided as they produce an adverse effect on many elements. The stock solutions are prepared at concentrations of 1,000 mg of the metal per liter. Commercially available standard solutions may also be used. Where the sample viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition (MSA) may be used (see Step 8.7).

5.7 Calibration standards - For those instruments which do not read out directly in concentration, a calibration curve is prepared to cover the appropriate concentration range. Usually, this means the preparation of standards which produce an absorbance of 0.0 to 0.7. Calibration standards are prepared by diluting the stock metal solutions at the time of analysis. For best results, calibration standards should be prepared fresh each time a batch of samples is analyzed. Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range of the linear part of the curve. The calibration standards should be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following processing. Beginning with the blank and working toward the highest standard, aspirate the solutions and record the readings. Repeat the operation with both the calibration standards and the samples a sufficient number of times to secure a reliable average reading for each solution. Calibration standards for furnace procedures should be prepared as described on the individual sheets for that metal. Calibration curves are always required.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material in Chapter Three, Metallic Analytes.

7.0 PROCEDURE

7.1 Preliminary treatment of waste water, ground water, EP extracts, and industrial waste is always necessary because of the complexity and variability of sample matrices. Solids, slurries, and suspended material must be subjected to a solubilization process before analysis. This process may vary because of the metals to be determined and the nature of the sample being analyzed. Solubilization and digestion procedures are presented in Chapter Three, Step 3.2, Sample Preparation Methods. Samples which are to be analyzed for dissolved constituents need not be digested if they have been filtered and acidified.

7.2 Direct aspiration (flame) procedure

7.2.1 Differences between the various makes and models of satisfactory atomic absorption spectrophotometers prevent the formulation of detailed instructions applicable to every instrument. The analyst should follow the manufacturer's operating instructions for a particular

instrument. In general, after choosing the proper lamp for the analysis, allow the lamp to warm up for a minimum of 15 minutes, unless operated in a double-beam mode. During this period, align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width, and adjust the current according to the manufacturer's recommendation. Subsequently, light the flame and regulate the flow of fuel and oxidant. Adjust the burner and nebulizer flow rate for maximum percent absorption and stability. Balance the photometer. Run a series of standards of the element under analysis. Construct a calibration curve by plotting the concentrations of the standards against absorbances. Set the curve corrector of a direct reading instrument to read out the proper concentration. Aspirate the samples and determine the concentrations either directly or from the calibration curve. Standards must be run each time a sample or series of samples is run.

7.3 Furnace procedure

7.3.1 Furnace devices (flameless atomization) are a most useful means of extending detection limits. Because of differences between various makes and models of satisfactory instruments, no detailed operating instructions can be given for each instrument. Instead, the analyst should follow the instructions provided by the manufacturer of a particular instrument.

7.3.2 Background correction is important when using flameless atomization, especially below 350 nm. Certain samples, when atomized, may absorb or scatter light from the lamp. This can be caused by the presence of gaseous molecular species, salt particles, or smoke in the sample beam. If no correction is made, sample absorbance will be greater than it should be, and the analytical result will be erroneously high. Zeeman background correction is effective in overcoming composition or structured background interferences. It is particularly useful when analyzing for As in the presence of Al and when analyzing for Se in the presence of Fe.

7.3.3 Memory effects occur when the analyte is not totally volatilized during atomization. This condition depends on several factors: volatility of the element and its chemical form, whether pyrolytic graphite is used, the rate of atomization, and furnace design. This situation is detected through blank burns. The tube should be cleaned by operating the furnace at full power for the required time period, as needed, at regular intervals during the series of determinations.

7.3.4 Inject a measured microliter aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.3.5 To verify the absence of interference, follow the serial dilution procedure given in Step 8.6.

7.3.6 A check standard should be run after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced. Tube life depends on sample matrix and atomization temperature. A conservative estimate would be that a tube will last at least 50 firings. A pyrolytic coating will extend that estimated life by a factor of three.

7.4 Calculation

7.4.1 For determination of metal concentration by direct aspiration and furnace: Read the metal value from the calibration curve or directly from the read-out system of the instrument.

7.4.2 If dilution of sample was required:

$$\text{ug / L metal in sample} = A\,\frac{(C + B)}{C}$$

where:

A = ug/L of metal in diluted aliquot from calibration curve.
B = Acid blank matrix used for dilution, mL.
C = Sample aliquot, mL.

7.4.3 For solid samples, report all concentrations in consistent units based on wet weight. Hence:

$$\text{ug metal / kg sample} = \frac{A \times V}{W}$$

where:

A = ug/L of metal in processed sample from calibration curve.
V = Final volume of the processed sample, mL.
W = Weight of sample, grams.

7.4.4 Different injection volumes must not be used for samples and standards. Instead, the sample should be diluted and the same size injection volume be used for both samples and standards. If dilution of the sample was required:

$$\text{ug / L of metal in sample} = Z\,\frac{(C + B)}{C}$$

where:

Z = ug/L of metal read from calibration curve or read-out system.
B = Acid blank matrix used for dilution mL.
C = Sample aliquot, mL.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 A calibration curve must be prepared each day with a minimum of a calibration blank and three standards. After calibration, the calibration curve must be verified by use of at least a calibration blank and a calibration check standard (made from a reference material or other independent standard material) at or near the mid-range. The calibration reference standard must be measured within 10 % of its true value for the curve to be considered valid.

8.3 If more than 10 samples per day are analyzed, the working standard curve must be verified by measuring satisfactorily a mid-range standard or reference standard after every 10 samples. This sample value must be within 20% of the true value, or the previous ten samples need to be reanalyzed.

8.4 At least one matrix spike and one matrix spike duplicate sample shall be included in each analytical batch. A laboratory control sample shall also be processed with each sample batch. Refer to Chapter One for more information.

8.5 Where the sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition (MSA) is recommended (see Section 8.7 below). Section 8.6 provides tests to evaluate the need for using the MSA.

8.6 Interference tests

8.6.1 Dilution test - For each analytical batch select one typical sample for serial dilution to determine whether interferences are present. The concentration of the analyte should be at least 25 times the estimated detection limit. Determine the apparent concentration in the undiluted sample. Dilute the sample by a minimum of five fold (1 + 4) and reanalyze. If all of the samples in the batch are below 10 times the detection limits, perform the spike recovery analysis described below. Agreement within 10% between the concentration for the undiluted sample and five times the concentration for the diluted sample indicates the absence of interferences, and such samples may be analyzed without using the method of standard additions.

8.6.2 Recovery test - If results from the dilution test do not agree, a matrix interference may be suspected and a spiked sample should be analyzed to help confirm the finding from the dilution test. Withdraw another aliquot of the test sample and add a known amount of analyte to bring the concentration of the analyte to 2 to 5 times the original concentration. If all of the samples in the batch have analyte concentrations below the detection limit, spike the selected sample at 20 times the detection limit. Analyze the spiked sample and calculate the spike recovery. If the recovery is less than 85% or greater than 115%, the method of standard additions shall be used for all samples in the batch.

8.7 Method of standard additions - The standard addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The method of standard additions shall be used for analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

8.7.1 The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a known volume V_S of a standard analyte solution of concentration C_S. To the second aliquot (labeled B) is added the same volume V_S of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration C_x is calculated:

$$C_X = \frac{S_B V_S C_S}{(S_A - S_B) V_X}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_s and C_s should be chosen so that S_A is roughly twice S_B on the average, avoiding excess dilution of the sample. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

8.7.2 Improved results can be obtained by employing a series of standard additions. To equal volumes of the sample are added a series of standard solutions containing different known quantities of the analyte, and all solutions are diluted to the same final volume. For example, addition 1 should be prepared so that the resulting concentration is approximately 50 percent of the expected absorbance from the endogenous analyte in the sample. Additions 2 and 3 should be prepared so that the concentrations are approximately 100 and 150 percent of the expected endogenous sample absorbance. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated to zero absorbance, the point of interception of the abscissa is the endogenous concentration of the analyte in the sample. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Figure 1. A linear regression program may be used to obtain the intercept concentration.

8.7.3 For the results of this MSA technique to be valid, the following limitations must be taken into consideration:

1. The apparent concentrations from the calibration curve must be linear over the concentration range of concern. For the best results, the slope of the MSA plot should be nearly the same as the slope of the standard curve. If the slope is significantly different (greater than 20%), caution should be exercised.

2. The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.

3. The determination must be free of spectral interference and corrected for nonspecific background interference.

8.8 All quality control measures described in Chapter One should be followed.

9.0 METHOD PERFORMANCE

9.1 See individual methods.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.

2. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

3. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

TABLE 1.
ATOMIC ABSORPTION CONCENTRATION RANGES

Metal	Direct Aspiration Detection Limit (mg/L)	Direct Aspiration Sensitivity (mg/L)	Furnace Procedure[a,c] Detection Limit (ug/L)
Aluminum	0.1	1	--
Antimony	0.2	0.5	3
Arsenic[b]	0.002	--	1
Barium	0.1	0.4	2
Beryllium	0.005	0.025	0.2
Cadmium	0.005	0.025	0.1
Calcium	0.01	0.08	--
Chromium	0.05	0.25	1
Cobalt	0.05	0.2	1
Copper	0.02	0.1	1
Iron	0.03	0.12	1
Lead	0.1	0.5	1
Lithium	0.002	0.04	--
Magnesium	0.001	0.007	--
Manganese	0.01	0.05	0.2
Mercury[d]	0.0002	--	--
Molybdenum(p)	0.1	0.4	1
Nickel	0.04	0.15	--
Osmium	0.03	1	--
Potassium	0.01	0.04	--
Selenium[b]	0.002	--	2
Silver	0.01	0.06	0.2
Sodium	0.002	0.015	--
Strontium	0.03	0.15	--
Thallium	0.1	0.5	1
Tin	0.8	4	--
Vanadium(p)	0.2	0.8	4
Zinc	0.005	0.02	0.05

NOTE: The symbol (p) indicates the use of pyrolytic graphite with the furnace procedure.

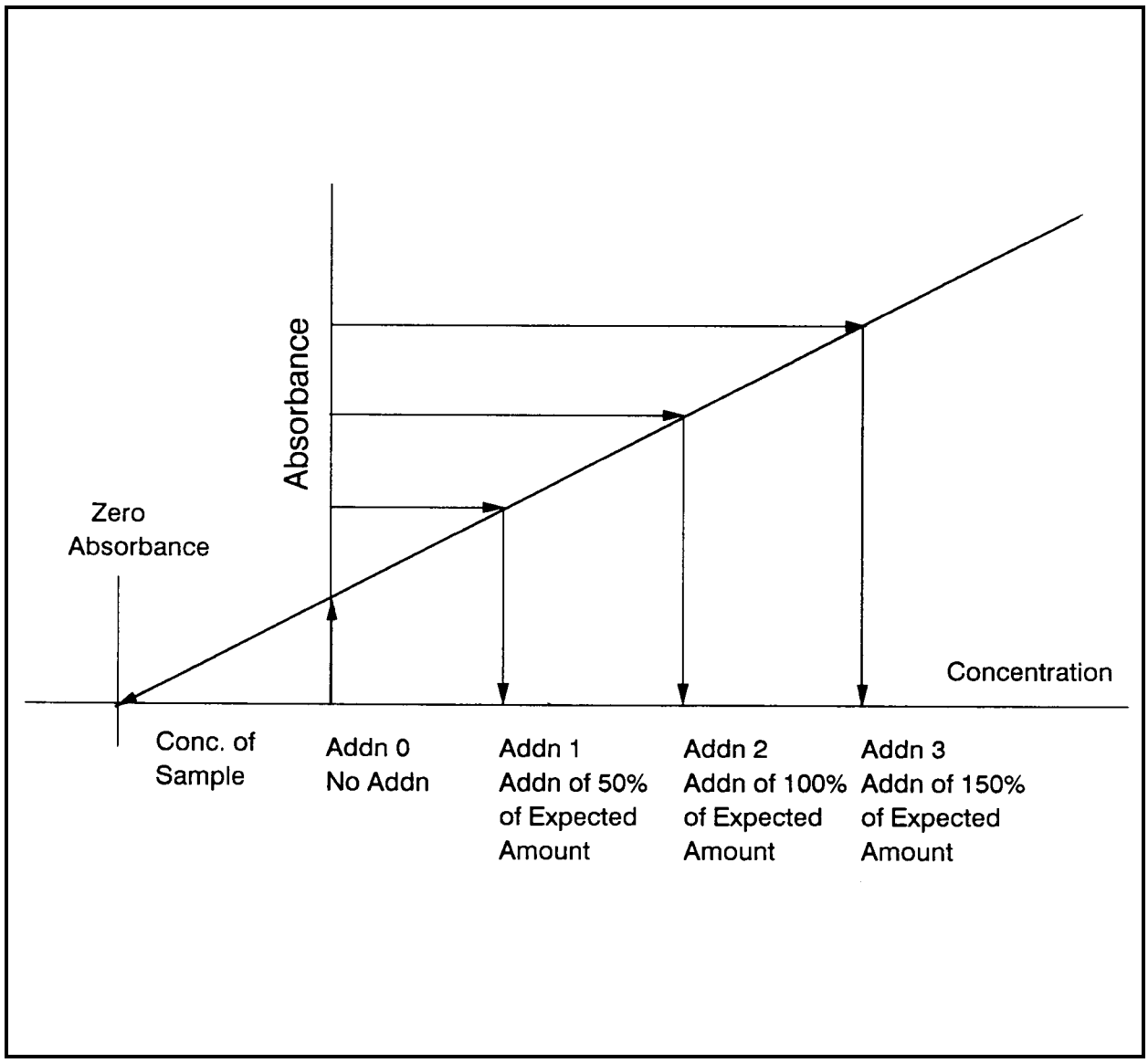
[a]For furnace sensitivity values, consult instrument operating manual.

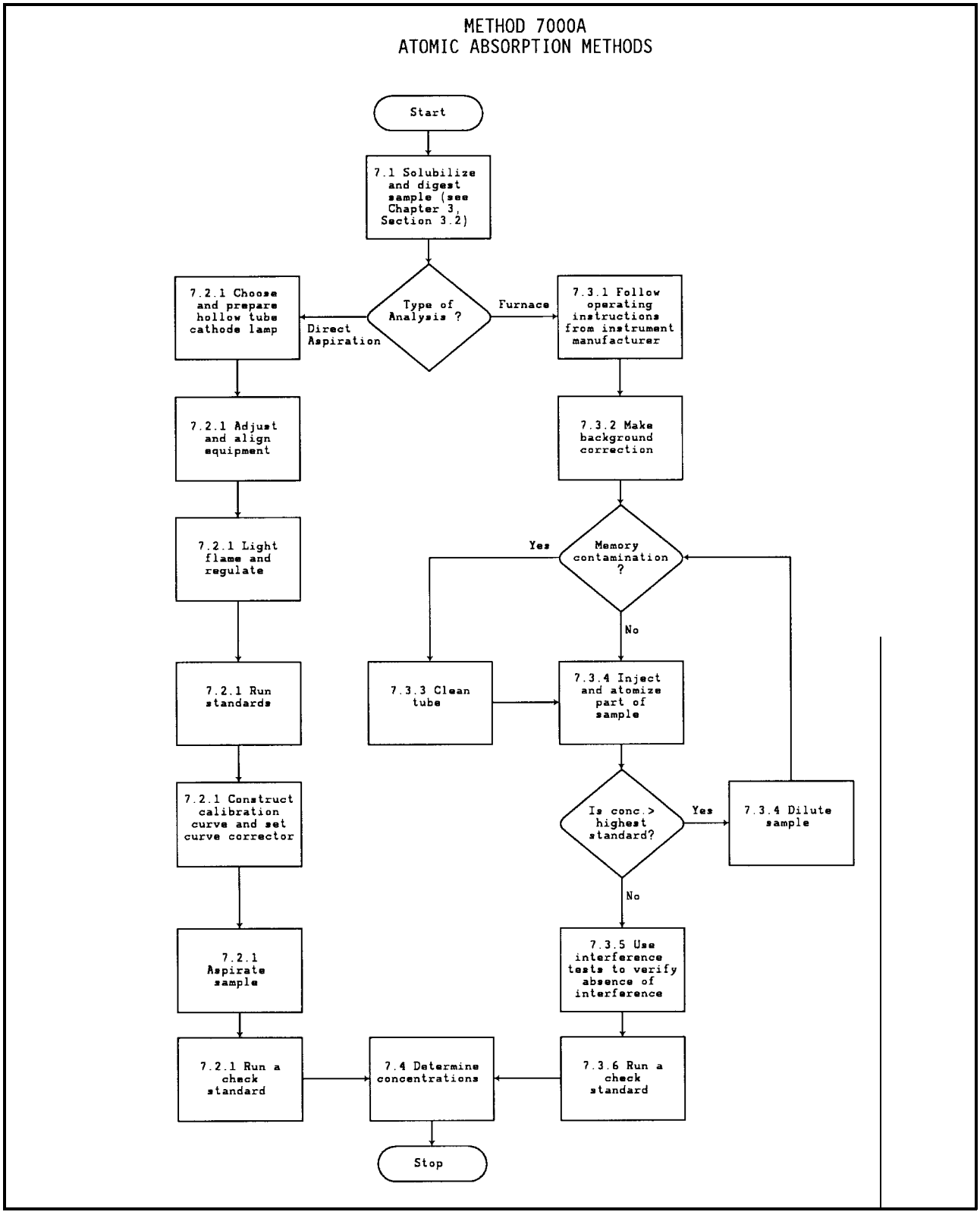
[b]Gaseous hydride method.

[c]The listed furnace values are those expected when using a 20-uL injection and normal gas flow, except in the cases of arsenic and selenium, where gas interrupt is used.

[d]Cold vapor technique.

FIGURE 1.
STANDARD ADDITION PLOT




METHOD 7000A
ATOMIC ABSORPTION METHODS
Start
7.1 Solubilize and digest sample (see Chapter 3, Section 3.2)
Type of Analysis ?
Direct Aspiration
Furnace
7.2.1 Choose and prepare hollow tube cathode lamp
7.3.1 Follow operating instructions from instrument manufacturer
7.2.1 Adjust and align equipment
7.3.2 Make background correction
7.2.1 Light flame and regulate
Memory contamination ?
Yes
No
7.2.1 Run standards
7.3.3 Clean tube
7.3.4 Inject and atomize part of sample
7.2.1 Construct calibration curve and set curve corrector
Is conc.> highest standard?
Yes
7.3.4 Dilute sample
No
7.2.1 Aspirate sample
7.3.5 Use interference tests to verify absence of interference
7.2.1 Run a check standard
7.4 Determine concentrations
7.3.6 Run a check standard
Stop

METHOD 8000B

DETERMINATIVE CHROMATOGRAPHIC SEPARATIONS

1.0 SCOPE AND APPLICATION

1.1 Method 8000 is not a determinative method but instead provides guidance on analytical chromatography and describes calibration and quality control requirements that are common to all SW-846 chromatographic methods. Apply Method 8000 in conjunction with all SW-846 determinative chromatographic methods. The methods include, but are not limited to, the following:

Method Number	Analytes	Chromatographic Technique (see Sec. 1.5)	Detector
7580	White phosphorus (P_4)	GC, capillary column	NPD
8011	EDB, DBCP	GC, capillary column	ECD
8015	Nonhalogenated volatiles	GC, packed & capillary column	FID
8021	Volatiles	GC, capillary column	PID, ELCD
8031	Acrylonitrile	GC, packed column	NPD
8032	Acrylamide	GC, packed column	ECD
8033	Acetonitrile	GC, capillary column	NPD
8041	Phenols	Underivatized or derivatized, GC, capillary column	FID, ECD
8061	Phthalates	GC, capillary column	ECD
8070	Nitrosamines	GC, packed column	NPD, ELCD, TED
8081	Organochlorine pesticides	GC, capillary column	ECD, ELCD
8082	Polychlorinated biphenyls	GC, capillary column	ECD, ELCD
8091	Nitroaromatics and cyclic ketones	GC, capillary column	ECD
8100	PAHs	GC, packed & capillary column	FID
8111	Haloethers	GC, capillary column	ECD
8121	Chlorinated hydrocarbons	GC, capillary column	ECD

[52]*Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods*, SW-846, Third Edition**,** Final Update III (December 1996), Method 8000B, pp. 1-46. (Reprinted in its entirety from CD-ROM.)

Method Number	Analytes	Chromatographic Technique (see Sec. 1.5)	Detector
8131	Aniline and selected derivatives	GC, capillary column	NPD
8141	Organophosphorus pesticides	GC, capillary column	FPD, NPD, ELCD
8151	Acid herbicides	Derivatize; GC, capillary column	ECD
8260	Volatiles	GC, capillary column	MS
8270	Semivolatiles	GC, capillary column	MS
8275	Semivolatiles	Thermal extraction/GC	MS
8280	Dioxins and Dibenzofurans	GC, capillary column	Low resolution MS
8290	Dioxins and Dibenzofurans	GC, capillary column	High resolution MS
8310	PAHs	HPLC, reverse phase	UV, Fluorescence
8315	Carbonyl compounds	Derivatize; HPLC	Fluorescence
8316	Acrylamide, acrylonitrile, acrolein	HPLC, reverse phase	UV
8318	N-Methyl carbamates	Derivatize; HPLC	Fluorescence
8321	Extractable nonvolatiles	HPLC, reverse phase	TS/MS, UV
8325	Extractable nonvolatiles	HPLC, reverse phase	PB/MS, UV
8330	Nitroaromatics and nitramines	HPLC, reverse phase	UV
8331	Tetrazene	HPLC, ion pair, reverse phase	UV
8332	Nitroglycerine	HPLC, reverse phase	UV
8410	Semivolatiles	GC, capillary column	FT-IR
8430	Bis(2-chloroethyl) ether hydrolysis products	GC, capillary column	FT-IR

DBCP = Dibromochloropropane
ECD = Electron capture detector
EDB = Ethylene dibromide
ELCD = Electrolytic conductivity detector
FID = Flame ionization detector
FPD = Flame photometric detector
FT-IR = Fourier transform-infrared
GC = Gas chromatography
HPLC = High performance liquid chromatography
MS = Mass spectrometry
NPD = Nitrogen/phosphorous detector
PAHs = Polynuclear aromatic hydrocarbons
PB/MS = Particle beam mass spectrometry
PID = Photoionization detector
TED = Thermionic emission detector
TS/MS = Thermospray mass spectrometry
UV = Ultraviolet

1.2 Analytical chromatography is used to separate target analytes from co-extracted interferences in samples. Chromatographic methods can be divided into two major categories: gas chromatography (GC) and high performance liquid chromatography (HPLC).

1.2.1 Gas chromatography (more properly called gas-liquid chromatography) is the separation technique of choice for organic compounds which can be volatilized without being decomposed or chemically rearranged.

1.2.2 High performance liquid chromatography (HPLC) is a separation technique useful for semivolatile and nonvolatile chemicals or for analytes that decompose upon heating. Successful liquid chromatographic separation requires that the analyte(s) of interest be soluble in the solvent(s) selected for use as the mobile phase. Because the solvents are delivered under pressure, the technique was originally designated as high pressure liquid chromatography, but now is commonly referred to as high performance liquid chromatography.

1.3 All chromatographic processes achieve separation by passing a mobile phase over a stationary phase. Constituents in a mixture are separated because they partition differently between the mobile and stationary phases and thus have different retention times. Compounds that interact strongly with the stationary phase elute slowly (i.e., long retention time), while compounds that remain in the mobile phase elute quickly (i.e., short retention time).

1.3.1 The mobile phase for GC is an inert gas, usually helium, and the stationary phase is generally a silicone oil or similar material.

1.3.2 In "normal phase" HPLC, the mobile phase is less polar than the stationary phase. In "reverse phase" HPLC, the converse is true. Reverse phase HPLC is the technique of choice for environmental and waste analyses of non-volatile organic target analytes.

1.4 A number of specific GC and LC techniques are used for environmental and waste analyses. The specific techniques are distinguished by the chromatographic hardware or by the chemical mechanisms used to achieve separations.

1.4.1 GC methods, including those in SW-846, can be categorized on the basis of the chromatographic columns employed.

1.4.1.1 Packed columns are typically made from glass or stainless steel tubing and generally are 1.5 - 3 m long with a 2 - 4 mm ID, and filled with small particles (60-100 mesh diatomaceous earth or carbon) coated with a liquid phase.

1.4.1.2 Capillary columns are typically made from open tubular glass capillary columns that are 15 - 100 m long with a 0.2 - 0.75 mm ID, and coated with a liquid phase. Most capillary columns are now made of fused silica, although glass columns are still sold for the analysis of volatiles. Capillary columns are inherently more efficient than packed columns and have replaced packed columns for most SW-846 applications.

1.4.2 SW-846 HPLC methods are categorized on the basis of the mechanism of separation.

1.4.2.1 Partition chromatography is the basis of reverse phase HPLC separations.

Analytes are separated on a hydrophobic column using a polar mobile phase pumped at high pressure (800 - 4000 psi) through a stainless steel column 10 - 25 cm long with a 2 - 4 mm ID and packed with 3 - 10 µm silica or divinyl benzene-styrene particles.

1.4.2.2 Ion exchange chromatography is used to separate ionic species.

1.5 SW-846 methods describe columns and conditions that have been demonstrated to provide optimum separation of all or most target analytes listed in that specific procedure. Most often, those columns were the ones used by EPA during method development and testing. Analysts may change those columns and conditions, provided that they demonstrate performance for the analytes of interest that is appropriate for the intended application. This is especially true when limited groups of analytes are to be monitored (i.e., if only a subset of the list of target analytes in a method are required, then the chromatographic conditions and columns may be optimized for those analytes).

1.5.1 Chromatographic performance is demonstrated by the resolution of standards and the ability to model the response of the detector during calibration, and by the sensitivity, accuracy, precision, frequency of false positives, and frequency of false negatives during analysis. The laboratory must demonstrate that an alternate chromatographic procedure provides performance that satisfies the analytical requirements of the specific application for which it is being used. Such demonstrations should be performed using the procedures outlined in Secs. 8.2 to 8.5 of this method and those in Chapter
One.

1.5.2 In addition, laboratories must be cautious whenever the use of two dissimilar columns is included in a method for confirmation of identification. For instance, a DB-5 column generally cannot be used for confirmation of results obtained using an SPB-5 column because the stationary phases are not sufficiently dissimilar and the changes in elution order (if any) will not provide adequate confirmation.

1.6 When gas chromatographic conditions are changed, retention times and analytical separations are often affected. For example, increasing the GC oven temperature changes the partitioning between the mobile and stationary phases, leading to shorter retention times. GC retention times can also be changed by selecting a column with a different length, stationary-phase loading (i.e., capillary film thickness or percent loading for packed columns), or alternate liquid phase. As a result, two critical aspects of any SW-846 chromatographic method are the determination and/or verification of retention times and analyte separation.

1.7 HPLC retention times and analytical separations are also affected by changes in the mobile and stationary phases. The HPLC mobile phase is easily changed by adjusting the composition of the solvent mixture being pumped through the column. In reverse phase HPLC, increasing the ratio of methanol (or acetonitrile) to water shortens retention times. HPLC retention times can also be changed by selecting a column with (1) a different length, (2) an alternate bonded phase, or (3) a different particle size (e.g., smaller particles generally increase column resolution). SW-846 methods provide conditions that have been demonstrated to provide good HPLC separations using specific instruments to analyze a limited number of samples. Analysts (particularly those using HPLC/MS) may need to tailor the chromatographic conditions listed in the method for their specific application and/or instrument. HPLC methods are particularly sensitive to small changes in chromatographic conditions, including temperature. HPLC column temperature control ovens should be used to maintain constant retention times since ambient laboratory temperatures often fluctuate throughout the course of a day.

1.8 Chromatographic methods can be used to produce data of appropriate quality for the analysis of environmental and waste samples. However, data quality can be greatly enhanced when the analyst understands both the intended use of the results and the limitations of the specific analytical procedures being employed. Therefore, these methods are recommended for use only by, or under the close supervision of, experienced analysts. Many difficulties observed in the performance of SW-846 methods for the analysis of RCRA wastes can be attributed to the lack of skill and training of the analyst.

1.8.1 Methods using selective (e.g., PID, NPD, ELCD) or non-selective (e.g., FID) detectors may present serious difficulties when used for site investigations, including co-elution of target analytes, false negatives due to retention time shifts, and false positives and quantitation errors due to co-eluting non-target sample components.

1.8.2 In contrast, GC methods employing selective or non-selective detectors may be appropriate for remediation activities where the analytes of concern are known, of limited number, and of significantly greater concentration than potentially interfering materials.

1.8.3 If the site is not well characterized, and especially if large numbers of target analytes are of concern, analysis by GC/MS or HPLC/MS may be more appropriate.

1.9 Each of the chromatographic methods includes a list of the compounds that it may be used to determine. The lists in some methods are lengthy and it may not be practical or appropriate to attempt to determine all the analytes simultaneously. Such analyte lists do not imply a regulatory requirement for the analysis of any or all of the compounds, but rather, indicate the method(s) which may be applicable to those analytes.

1.10 Prior to employing this method, analysts are advised to consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in this procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to meet the data quality objectives or needs for the intended use of the data.

2.0 SUMMARY OF METHOD

Method 8000 describes general considerations in achieving chromatographic separations and performing calibrations. Method 8000 is to be used in conjunction with all SW-846 determinative chromatographic methods including, but not limited to, each method listed in Sec.1.1. Each of these chromatographic methods recommends appropriate procedures for sample preparation, extraction, cleanup, or derivatization. Consult the specific procedures for additional information on these crucial steps in the analytical process.

2.1 Sec. 3.1 of this method provides general guidance on minimizing contamination, including cross-contamination between samples. Sample screening procedures are strongly recommended, and discussed in Sec. 3.2.

2.2 Before any sample or blank is introduced into a chromatographic system, the appropriate resolution criteria and calibration procedure(s) described in Method 8000 must be satisfied (see Secs. 3.3 and 8.3).

2.3 Secs. 3.4 and 3.5 provide information on the effects of chromatographic interferences.

2.4 Sec 4.0 of this method contains generalized specifications for the components of both GC and HPLC systems used in SW-846 analyses.

2.5 Calibration of the analytical system is another critical step in the generation of quality data. Sec. 7.5 discusses specific procedures and calculations for both linear and non-linear calibration relationships. The continued use of any chromatographic procedure requires a verification of the calibration relationship, and procedures for such verifications are described in this method as well (see Sec. 7.7).

2.6 The identification of target compounds by any chromatographic procedure is based, at least in part, on retention times. Sec. 7.6 provides procedures for the determination of retention times and retention time windows to be used with the specific methods listed in Sec. 1.1.

2.7 The calculations necessary to derive sample-specific concentration results from the instrument responses are common to most of the analytical methods listed in Sec. 1.1. Therefore, Sec. 7.10 of Method 8000 contains a summary of the commonly used calculations.

2.8 Preventive maintenance and corrective actions are essential to the generation of quality data in a routine laboratory setting. Suggestions for such procedures are found in Sec. 7.11.

2.9 Most of the methods listed in Sec. 1.1 employ a common approach to quality control (QC). While some of the overall procedures are described in Chapter One, Sec. 8.0 describes routinely used procedures for calibration verification, instrument performance checks, demonstrating acceptable performance, etc.

2.10 Before performing analyses of specific samples, analysts should determine acceptable recovery ranges for all target analytes of interest in the type of matrices to be tested. These procedures are described in Secs. 8.4, 8.5, and 8.7. Analysts must also be able to demonstrate that the sensitivity of the procedure employed is appropriate for the intended application. One approach to such a demonstration is to estimate the method detection limits for the analytes of interest using the procedures in Chapter One.

3.0 INTERFERENCES/CHROMATOGRAPHIC PERFORMANCE

3.1 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed in sequence. To reduce the potential for carryover, the sample syringe or purging device must be thoroughly rinsed between samples with an appropriate solvent. Purge and trap devices or headspace devices should be thoroughly baked out between samples. Where practical, samples with unusually high concentrations of analytes should be followed by a solvent blank or by an analysis of organic-free reagent water to check for cross-contamination. If the target compounds present in an unusually concentrated sample are also found to be present in the subsequent samples, the analyst must demonstrate that the compounds are not due to carryover. Conversely, if those target compounds are <u>not</u> present in the subsequent sample, then the analysis of a solvent blank or organic-free reagent water is not necessary.

Purging vessels may be cleaned by rinsing with methanol, followed by a distilled water rinse and drying in a 105°C oven between analyses. Detergent solutions may also be used, but care must be taken to remove the detergent residue from the purging vessel. Other approaches to cleaning purging vessels may also be employed, provided that the laboratory can demonstrate that they are effective in removing contaminants.

3.2 In addition to carryover of compounds from one sample to the next, the analysis of high-concentration samples can lead to contamination of the analytical instrument itself. This is particularly true for GC/MS. Eliminating this contamination can require significant time and effort in cleaning the instruments, time that cannot be spent analyzing samples. The most reliable procedure for ensuring minimum down time during the GC/MS analysis of samples is to screen samples by some other technique. Samples to be analyzed for volatiles can be screened using an automated headspace sampler (Method 5021) connected to a GC/PID/ELCD detector (Method 8021). Samples to be analyzed for semivolatiles can be screened using GC/FID. Other screening methods are also acceptable. The analyst should use the screening results to choose an appropriate dilution factor for the GC/MS analysis that will prevent system contamination yet still provide adequate sensitivity for the major constituents of the sample.

3.3 One of the most important measures of chromatographic performance is resolution, the separation of chromatographic peaks (peak separation/average peak width). Peak separations are facilitated by good column efficiency (i.e., narrow peak widths) and good column selectivity (i.e., analytes partition differently between the mobile and stationary phases).

3.3.1 The goal of analytical chromatography is to separate sample constituents within a reasonable time. Baseline resolution of each target analyte from co-extracted materials provides the best quantitative results, but is not always possible to achieve.

3.3.2 In general, capillary columns contain a greater number of theoretical plates than packed columns. (A theoretical plate is a surface at which an interaction between the sample components and the stationary phase may occur). As a result, capillary columns generally provide more complete separation of the analytes of interest. However, packed columns can provide adequate resolution of some analytes and are most appropriately employed when the list of analytes to be determined is relatively short.

3.3.3 The ability to resolve individual compounds is generally the limiting factor for the number of analytes that can be measured using a single procedure. Some procedures, particularly Method 8081 (Organochlorine Pesticides), Method 8082 (PCBs), and Method 8141 (Organophosphorus Pesticides), list analytes that may not all be resolved from one another. Therefore, while each of these methods is suitable for the listed compounds, they may not be suitable to measure the entire list in a single analysis. In addition, some methods include analytes that are isomers or closely related compounds which are well-known as co-eluting or are not completely separable. In these instances, the results should be reported as the sum of the two (or more) analytes. Laboratories should demonstrate that target analytes are resolved during calibration and satisfy the requirements in Sec. 8.3, or should report the results as "totals" or "sums" (e.g., m + p-xylene). Methods that utilize mass spectrometry for detection are less affected by resolution problems, because overlapping peaks may often be mass-resolved. However, even mass spectrometry will not be able to mass resolve positional isomers such as m-xylene and p-xylene if the compounds co-elute.

3.4 Elevated chromatographic baselines should be minimized or eliminated during these analyses. Baseline humps can usually be reduced or eliminated by the application of appropriate sample clean-up (see Method 3600), extract dilution, the use of pre-columns and/or inserts, or use of a selective detector. Integration of "hump-o-grams" can result in significant quantitative errors. When elevated baselines are observed during the analysis of blanks and standards, the chromatographic system should be considered contaminated. This contamination may be the result of impure carrier gas, inadequate gas conditioning, septum bleed, column oxidation, and/or pyrolysis products in the injector or column. Such contamination is unacceptable and should be addressed through a program of preventive maintenance and corrective action.

3.5 GC preventive maintenance and corrective action

Poor GC performance may be expected whenever a chromatographic system is contaminated with high-boiling materials, particularly in the injector. Analysts should perform routine maintenance, including replacement of septa, cleaning and deactivating injector liners, and removing as much as 0.5 - 1 m from the injector side of a capillary column.

If chromatographic performance or ghost peaks are still a problem, cleaning of the metallic surfaces of the injection port itself may be necessary. Capillary columns are reliable and easy to use, but several specific actions are necessary to ensure good performance.

3.5.1 Contact between the capillary column and the wall of the GC oven can affect both chromatographic performance and column life. Care should be taken to prevent the column from touching the oven walls.

3.5.2 Care should be taken to keep oxygen out of capillary columns.

3.5.3 Septa should only be changed after the oven has cooled.

3.5.4 Columns should be flushed with carrier gas for 10 minutes before reheating the oven.

3.5.5 Carrier gas should be scrubbed to remove traces of oxygen and scrubbers should be changed regularly.

3.5.6 Carrier gas should always be passed through the column whenever the oven is heated.

3.6 HPLC preventive maintenance and corrective action

HPLC band broadening results from improper instrument setup or maintenance. Band broadening results whenever there is a dead volume between the injector and the detector. Therefore plumbing connections should be of minimum length and diameter, and ferrules should be properly positioned on the tubing to minimize dead volume.

3.6.1 Columns should not be subjected to sudden physical stress (e.g., dropping) or solvent shocks (e.g., changing solvents without a gradient).

3.6.2 Columns can become contaminated with particulates or insoluble materials. Guard columns should be used when dirty samples are analyzed.

3.6.3 High quality columns are packed uniformly with small uniform diameter particles with a minimum number of free silol groups. Use of such columns will result in optimum chromatographic performance.

3.6.4 Columns should be replaced when performance degrades (e.g., significant band broadening, peak splitting, or loss of chromatographic resolution occurs).

3.6.5 Pumping systems should deliver reproducible gradients at a uniform flow rate. Rates can be checked by collecting solvent into a graduated cylinder.

3.6.6 Column temperatures should be regulated by the use of column temperature control ovens to ensure reproducibility of retention times.

3.6.7 Small changes in the composition or pH of the mobile phase can have a significant effect on retention times.

4.0 APPARATUS AND MATERIALS

4.1 GC inlet systems

4.1.1 Volatile organics

Volatile organic analytes are introduced into a GC through a purge-and-trap system, by direct injection, or by other devices. The purge-and-trap apparatus is described in Method 5030 for water samples and in Method 5035 for soil and other solid samples. See Method 5000 for guidance on all forms of sample introduction of volatiles into the GC and GC/MS system.

4.1.2 Semivolatile organics

Sample extracts containing semivolatile organic compounds are introduced into a GC with a syringe that passes through a septum into an injection port. The injection port allows the sample extract to be vaporized prior to being flushed onto the GC column, hence the term "gas" chromatography. Correct set up and maintenance of the injector port is necessary to achieve acceptable performance with GC methods. Septa should be changed frequently enough to prevent retention time shifts of target analytes and peak tailing. The schedule for such septa changes is dependent on the quality of the septa, the sharpness of the needle, and the operation of the injection system. Appropriate injector liners should be installed, and liners should be cleaned and deactivated (with dichlorodimethylsilane) regularly.

4.1.3 Injector difficulties include the destruction of labile analytes and discrimination against high boiling compounds in capillary injectors.

4.1.3.1 Packed columns and wide-bore capillary columns (> 0.50 mm ID) should be mounted in 1/4-inch injectors. An injector liner is needed for capillary columns.

4.1.3.2 Narrow-bore capillary columns (≤ 0.32 mm ID) should be mounted in split/splitless (Grob-type) injectors. Split/splitless injectors require automated valve closures that direct most of the flow (and sample) onto the head of the analytical column. After 30 - 45 seconds, the split valve is opened, so that most of the flow is vented during analysis, thus eliminating the solvent tail, and maintaining proper flow through the column. The initial oven temperature should be below the boiling point of the injection solvent if the solvent front interferes with early eluting analytes or if the solvent effect is needed to resolve difficult-to-separate analytes.

4.1.3.3 Cool on-column injection allows the analysis of labile compounds that degrade on packed columns and in split/splitless injectors.

4.2 GC flow control

Precise control of the gas mobile phase is necessary to achieve reproducible GC retention times. Flow controllers within any GC used for SW-846 analyses must deliver a precisely metered gas flow at a rate appropriate for the GC column mounted in the instrument.

4.2.1 Most GCs have restrictors built into flow controllers. These restrictors are used to provide precise flow at the carrier gas flow rate specified in the method (e.g., use < 20 mL/min restrictors for wide-bore capillary methods). Carrier gas flow rates should be checked regularly (with both the injector and the oven heated) using a bubble meter or other appropriate procedure.

4.2.2 Cylinder pressures should also be regulated properly. Manifold pressures must be sufficiently large that a change in the head pressure of an individual instrument does not affect the flow through all instruments. Toggle valves that allow instruments to be isolated are recommended for all multi-instrument gas delivery systems. Analysts should spend time each week conducting preventative maintenance in order to ensure that proper flow control is maintained. One needs to search for leaks using a helium tester or soap solution at each connector in the gas delivery systems. Analysts should routinely conduct preventive maintenance activities, including those designed to ensure proper flow control and to identify potential leaks in the gas delivery system. The search for leaks may be conducted with a helium leak tester, soap solutions, performing static pressure tests, or other appropriate measures.

4.2.3 Carrier gas should be of high purity and should be conditioned between the cylinder and the GC to remove traces of water and oxygen. Scrubbers should be changed according to manufacturers recommendations. Gas regulators should contain stainless steel diaphragms. Neoprene diaphragms are a potential source of gas contamination, and should not be used.

4.3 Gas chromatographic columns

Each determinative method in SW-846 provides a description of a chromatographic column or columns with associated performance data. Other packed or capillary (open-tubular) columns may be substituted in SW-846 methods to improve performance if (1) the requirements of Secs. 8.3 and 8.4 are satisfied, and (2) target analytes are sufficiently resolved from one another and from co-extracted interferences to provide data of the appropriate quality for the intended application.

4.3.1 Narrower columns are more efficient (i.e., can resolve more analytes) but have a lower capacity (i.e., can accept less sample without peak distortion).

4.3.2 Longer columns can resolve more analytes, as resolution increases as a function of the square root of column length.

4.3.3 Increasing column film thickness or column loading increases column capacity and retention times.

4.3.4 Use of capillary columns has become standard practice in environmental and waste analysis. Capillary columns have an inherently greater ability to separate analytes than packed columns. However, packed columns can provide adequate resolution of some analytes and are most appropriately employed when the list of analytes to be determined is relatively short.

4.3.5 Columns used for SW-846 analyses should be installed properly. Column ends should be cut square. Contaminated ends should be trimmed off, and columns should be placed through ferrules before they are trimmed. Columns should not touch the walls of the GC oven during analysis, and the manufacturer's column temperature limits should not be exceeded.

4.3.6 Septa should be changed regularly and septum nuts should not be overtightened. Oxygen should not be introduced into a hot column and carrier gas should be passed through a column whenever it is heated. New columns, particularly packed columns, should be conditioned prior to analyzing samples.

4.4 GC detectors

Detectors are the transducers that respond to components that elute from a GC column and produce the electrical signal that is used for quantitative determinations. SW-846 analyses are conducted using selective detectors or mass spectrometers listed in Sec. 1.1. Except where otherwise recommended by the instrument manufacturer, selective non-MS detectors should be maintained at least 20°C above the highest oven temperature employed to prevent condensation and detector contamination. The transfer lines between the GC and an MS detector should be maintained at a temperature above the highest column temperature, or as specified by the instrument manufacturer, to prevent condensation.

4.5 HPLC injectors

Liquids are essentially non-compressible, so a mechanical device is necessary that allows introduction of the sample into a high pressure flow without significant disruption in the flow rate and hydraulic pressure. Normally, a 6-port valve is used for this purpose. A sample loop (generally 10-100 µL) is isolated from the flow of the mobile phase and filled with a sample extract. (Larger sample loops may be used to increase sensitivity, however, they may degrade chromatographic performance). The extract is then injected by turning the valve so that the mobile phase flows through the loop. This procedure virtually eliminates dead volume in the injector and is fully compatible with automated operation.

4.5.1 When the extract is highly viscous, a pressure spike results which can automatically shut off the HPLC pump.

4.5.2 Contamination of subsequent injections may occur when the extract contains material that is not soluble in the mobile phase.

4.5.3 Injection loops are easily changed but analysts must ensure that the compression fittings are properly installed to prevent leaks. Injectors require maintenance, as the surfaces that turn past each other do wear down.

4.6 HPLC pumps

The mobile phase used for HPLC must be accurately pressurized before it enters the injector. HPLC pumps are generally capable of delivering solvent at 5000 psi with excellent precision. The rate of delivery depends on the column that is used for the separation. Most environmental methods recommend flow rates of 0.25-1.0 mL/min. Flow rates should be checked by collecting column effluent in a graduated cylinder.

Most pumping systems are capable of changing solvent concentration during an analysis (i.e., gradient elution). Gradients are generated by either high pressure mixing of two streams between the pump and the

injector or by proportional mixing of the solvents before they are pumped. In either case, solvent mixing can cause changes in the solubility of dissolved gases, the formation of bubbles in the mobile phase, or non-reproducible gradients.

4.6.1 Air bubbles result in erratic baseline and, in the case of low pressure mixing, bubbles can cause the pump to cavitate. Therefore, HPLC solvents should be degassed prior to use.

4.6.2 Non-reproducible gradients can result in significant changes in retention times from run to run.

4.6.3 HPLC solvents should be filtered to remove particles that cause pump piston wear. HPLC pump maintenance includes replacing seals regularly. (Use of strong buffers or solvents like tetrahydrofuran can significantly shorten the lifetime of pump seals.) Pumps should deliver solvent with minimal pulsation.

4.7 HPLC Columns

These columns must be constructed with minimum dead volume and a narrow particle size distribution. HPLC columns are generally constructed of stainless steel tubing and are sealed with compression fittings. Manufacturers provide columns that are bonded with different alkyl groups (e.g., C_{18}, cyano, TMS), have different percent carbon loading, are packed with different particle sizes (3-10 µm), and are packed with particles of different pore size (smaller pores mean greater surface area), or are of different dimensions.

4.7.1 Columns with higher percent loading have the capacity to analyze somewhat larger samples, but extremely high loadings may contribute to problems with the particle beam MS interface.

4.7.2 Columns with free silol groups show less tailing of polar materials (e.g., amines).

4.7.3 A smaller particle (and pore) size generally gives better resolution, higher back pressure, and smaller sample capacity. Columns with 3 µm particle size may have short lifetimes when they are used for the analysis of complex waste extracts.

4.7.4 Improvements in column packing have resulted in 10 and 15 cm columns that provide the separating power necessary for most environmental and waste analyses.

4.7.5 Internal diameters of columns used for environmental and waste analysis are generally 2-5 mm. Narrower columns are called microbore columns. While they provide better separations, they become fouled more easily.

4.7.6 The lifetime and performance of HPLC columns can be improved through proper maintenance. Analysts should filter sample extracts, use compatible guard columns, check for clogged frits and for column voids. Columns should not be stored dry or containing strong buffers.

4.8 HPLC column temperature control ovens

HPLC retention times are much more reproducible if the column is held at a constant temperature. Temperature control ovens capable of maintaining the HPLC column at ± 0.1°C should be utilized to maintain consistent retention times throughout the course of an HPLC analysis. Normal oven operating temperature would be 3-5°C above ambient laboratory temperature.

4.9 HPLC detectors

Detectors are the transducers that respond to components that elute from a HPLC column and produce the electrical signal that is used for quantitative determinations. SW-846 analyses are conducted using selective detectors or mass spectrometers listed in Sec. 1.1. HPLC/MS requires the use of a sophisticated interface that separates target analytes from the aqueous mobile phase. Examples include the thermospray (TSP), electrospray (ESP), and the particle beam (PB) interfaces.

4.10 Data systems

Raw chromatographic data have to be reduced in order to provide the quantitative information required by analysts. The use of sophisticated data systems is strongly recommended for SW-846 chromatographic methods. The ability to store and replot chromatographic data is invaluable during data reduction and review. Organizations should establish their priorities and select the system that is most suitable for their applications.

4.11 Supplies

Chromatographers require a variety of supplies. The specific items that should be stocked depend on laboratory instrumentation and the analyses performed. At a minimum, laboratories need PTFE tape, stainless steel regulators, acid-washed copper tubing, and syringes, and replacement parts for instruments.

4.11.1 Laboratories performing GC analyses also require high purity gases, scrubbers for gas conditioning, gas-tight fittings, capillary cutters, magnifying glasses, septa with proper temperature limits, appropriate ferrules, dichlorodimethylsilane (for deactivating surfaces), glass wool, spare columns, and injection port liners.

4.11.2 Laboratories performing HPLC analyses require high purity solvents, column packing material, frits, 1/16-inch tubing, appropriate ferrules, solvent filtration apparatus, and solvent degassing apparatus.

5.0 REAGENTS

See the specific extraction and determinative methods for the reagents needed.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Refer to Chapter Four, Organic Analytes, Sec. 4.1, for information on sample collection, preservation and handling procedures. Additional information may be found in some of the individual sample extraction, preparation, and determinative methods.

7.0 PROCEDURE

Extraction and cleanup are critical for the successful analyses of environmental samples and wastes. Analysts should pay particular attention to selection of sample preparation procedures to obtain reliable measurements.

7.1 Extraction

The individual determinative methods for organic analytes in SW-846 often recommend appropriate sample extraction procedures. General guidance on semivolatile extraction procedures can be found in Method 3500. Guidance on volatile procedures can be found in Method 5000.

7.2 Cleanup and separation

The individual determinative methods for organic analytes in SW-846 often recommend appropriate cleanup procedures. General guidance on cleanup procedures can be found in Method 3600. While some relatively clean matrices (such as ground water samples) may not require extensive cleanups, the analyst should carefully balance the time savings gained by skipping cleanups against the potential increases in instrument down time and loss of data quality that can occur as a result.

7.3 Recommended chromatographic columns and instrument conditions are described in each determinative method. As noted earlier, these columns and conditions are typically those used during the development and testing of the method. However, other chromatographic systems may have somewhat different characteristics. In addition, analytical instrumentation continues to evolve. Therefore, SW-846 methods allow analysts some flexibility to change these conditions (with certain exceptions), as long as they demonstrate adequate performance.

Chromatographic performance is demonstrated by the resolution of standards and the ability to model the response of the detector during calibration, and by the sensitivity, accuracy, precision, frequency of false positives, and frequency of false negatives during analysis. If the laboratory employs an alternative chromatographic procedure or alternative conditions, then the laboratory must demonstrate that the performance satisfies the analytical requirements of the specific application for which the alternative chromatographic procedure is being used. Such demonstrations should be performed using the procedures outlined in Secs. 8.2 to 8.5 of this method and those in Chapter One.

7.4 Initial Calibration

Calibration of an analytical instrument involves the delineation of the relationship between the response of the instrument and the amount or concentration of an analyte introduced into the instrument. The graphical depiction of this relationship is often referred to as the calibration curve. In order to perform quantitative measurements, this relationship must be established prior to the analysis of any samples, and thus, is termed initial calibration.

Historically, many analytical methods have relied on linear models of the calibration relationship, where the instrument response is directly proportional to the amount of a target compound. The linear model has many advantages, among them, simplicity and ease of use. Unfortunately, given the advent of new detection techniques and the fact that many techniques cannot be optimized for all of the analytes to which they may be applied, the analyst is increasingly likely to encounter situations where the linear model neither applies nor is appropriate.

The initial calibration for SW-846 chromatographic methods involves the analysis of standards containing the target compounds at a minimum of five different concentrations covering the working range of the instrument. In order to produce acceptable sample results, the response of the instrument must be within the working range established by the initial calibration. The extrapolation of the calibration to concentrations above or below those of the actual calibration standards is <u>not</u> appropriate and may lead to significant quantitative errors regardless of the calibration model chosen. Analysts are advised that it may be necessary to prepare calibration standards that cover concentration ranges that are appropriate for specific projects or

type of analyses. For instance, the analyst should not necessarily expect to be able to perform a calibration appropriate for sub-ppb level analyses and also use the same calibration data for high-ppb or ppm level samples.

The specific options for evaluating the initial calibration are described in Sec. 7.5. The remainder of this section describes the preparation of calibration standards, the use of external and internal standard calibrations, and the calculation of both calibration factors and response factors.

7.4.1 Calibration standards are prepared using the procedures indicated in Sec. 5.0 of the determinative method of interest. However, the general procedure is described here.

7.4.1.1 For each analyte and surrogate of interest, prepare calibration standards at a minimum of five different concentrations by adding volumes of one or more stock standards to volumetric flasks and diluting to volume with an appropriate solvent.

7.4.1.2 The lowest concentration calibration standard that is analyzed during an initial calibration establishes the method quantitation limit based on the final volume of extract (or sample) described in the preparative method or employed by the laboratory.

7.4.1.3 The other concentrations should define the working range of the detector or correspond to the expected range of concentrations found in actual samples that are also within the working range of the detector.

7.4.1.4 For each analyte, at least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project, which may include establishing compliance with a regulatory or action limit.

7.4.1.5 Given the number of target compounds addressed by some of the methods listed in Sec. 1.1, it may be necessary to prepare several sets of calibration standards, each set consisting of five solutions at different concentrations. The initial calibration will then involve the analysis of each of these sets of five standards.

7.4.1.6 Once the standards have been prepared, the initial calibration begins by establishing chromatographic operating parameters that provide instrument performance equivalent to that documented in Sec. 7.0 of the determinative method of interest, or that is appropriate for the data quality objectives of the intended application.

7.4.2 External standard and internal standard calibration techniques

The chromatographic system may be calibrated using either the external standard or the internal standard techniques described below. General calibration criteria are provided in this section for GC and HPLC procedures using non-MS detection. The applicable calibration procedures for GC/MS (e.g., Methods 8260, 8270, 8280, and 8290), HPLC/MS (e.g., Methods 8321 and 8325), and GC/FT-IR (e.g., Method 8410) are described in those methods. Some determinative methods may provide special guidance on calibration that is specific to that method.

Regardless of whether external standard or internal standard calibration is used, introduce each calibration standard into the instrument using the same technique that is used to introduce the actual samples into the gas chromatograph (e.g., 1-3 µL injections for GC methods, 10-100 µL injections for HPLC methods, purge-and-trap techniques for volatiles, etc.). Tabulate peak area or height responses

against the mass or concentration injected, as described below.

7.4.2.1 External standard calibration procedure

External standard calibration involves comparison of instrument responses from the sample to the responses from the target compounds in the calibration standards. Sample peak areas (or peak heights) are compared to peak areas (or heights) of the standards. The ratio of the detector response to the amount (mass) of analyte in the calibration standard is defined as the calibration factor (CF).

$$CF = \frac{\text{Peak Area (or Height) of the Compound in the Standard}}{\text{Mass of the Compound Injected (in nanograms)}}$$

For multi-component analytes, see the appropriate determinative method for information on which areas to employ.

The CF can also be calculated using the concentration of the standard rather than the mass in the denominator of the equation above. However, the use of concentrations in CFs will require changes to the equations that are used to calculate sample concentrations (see Sec. 7.10.1.1).

7.4.2.2 Internal standard calibration procedure

Internal standard calibration involves the comparison of instrument responses from the target compounds in the sample to the responses of specific standards added to the sample or sample extract prior to injection. The ratio of the peak area (or height) of the target compound in the sample or sample extract to the peak area (or height) of the internal standard in the sample or sample extract is compared to a similar ratio derived for each calibration standard. The ratio is termed the response factor (RF), and may also be known as a relative response factor in other methods.

In many cases, internal standards are recommended in SW-846 methods. These recommended internal standards are often brominated, fluorinated, or stable isotopically labeled analogs of specific target compounds, or are closely related compounds whose presence in environmental samples is highly unlikely. If internal standards are not recommended in the method, then the analyst needs to select one or more internal standards that are similar in analytical behavior to the compounds of interest, and not expected to be found in the samples otherwise.

Whichever internal standards are employed, the analyst needs to demonstrate that the measurement of the internal standard is not affected by method analytes and surrogates or by matrix interferences. In general, internal standard calibration is not as useful for GC and HPLC methods with non-MS detectors because of the inability to chromatographically resolve many internal standards from the target compounds. The use of MS detectors makes internal standard calibration practical because the masses of the internal standards can be resolved from those of the target compounds even when chromatographic resolution cannot be achieved.

When preparing calibration standards for use with internal standard calibration, add the same amount of the internal standard solution to each calibration standard, such that the concentration of each internal standard is constant across all of the calibration standards, whereas

the concentrations of the target analytes will vary. The internal standard solution will contain one or more internal standards and the concentration of the individual internal standards may differ within the spiking solution (e.g., not all internal standards need to be at the same concentration in this solution). The mass of each internal standard added to each sample extract immediately prior to injection into the instrument or to each sample prior to purging must be the same as the mass of the internal standard in each calibration standard. The volume of the solution spiked into sample extracts should be such that minimal dilution of the extract occurs (e.g., 10 µL of solution added to a 1 mL final extract results in only a negligible 0.1% change in the final extract volume which can be ignored in the calculations).

An ideal internal standard concentration would yield a response factor of 1 for each analyte. However, this is not practical when dealing with more than a few target analytes. Therefore, as a general rule, the amount of internal standard should produce an instrument response (e.g., area counts) that is no more than 100 times that produced by the lowest concentration of the least responsive target analyte associated with the internal standard. This should result in a minimum response factor of approximately 0.01 for the least responsive target compound.

For each of the initial calibration standards, calculate the RF values for each target compound relative to one of the internal standards as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak area (or height) of the analyte or surrogate.
A_{is} = Peak area (or height) of the internal standard.
C_s = Concentration of the analyte or surrogate, in µg/L.
C_{is} = Concentration of the internal standard, in µg/L.

Note that in the equation above, RF is unitless, i.e., the units from the two area terms and the two concentration terms cancel out. Therefore, units other than µg/L may be used for the concentrations of the analyte, surrogate, and internal standard, provided that both C_s and C_{is} are expressed in the same units. The mass of the analyte and internal standard may also be used in calculating the RF value.

7.5 Calibration linearity

SW-846 chromatographic methods allow the use of both linear and non-linear models for the calibration data, as described below. Given the limitations in instrument data systems, it is likely that the analyst will have to choose one model for all analytes in a particular method. Both models can be applied to either external or internal standard calibration data.

NOTE: The option for non-linear calibration may be necessary to achieve low detection limits or to address specific instrumental techniques. However, it is not EPA's intent to allow non-linear calibration to be used to compensate for detector saturation at higher concentrations or to avoid proper instrument maintenance.

Whichever calibration model is employed, a unique analyte or surrogate concentration must fall within

the calibration range. Samples with concentrations that exceed the calibration range must be diluted to fall within the range.

NOTE: The following sections describe various options for initial calibration and provide the calibration acceptance criteria used to evaluate each option. The criteria listed in these sections are designed for quantitation of trace level concentrations of the analytes of interest. If data of lesser quality will satisfy project-specific data needs, then less stringent criteria may be employed, provided that they are documented and approved in a project-specific QA project plan.

The choice of a specific calibration model should be made in one of two ways. The first is to begin with the simplest approach, the linear model through the origin, and progressing through the other options until the calibration acceptance criteria are met. The second approach is to use *a priori* knowledge of the detector response to choose the calibration model. Such knowledge may come from previous experience, knowledge of the physics of the detector, or specific manufacturer's recommendations.

7.5.1 Linear calibration using the average calibration or response factor

When calculated as described in Sec. 7.4, both calibration factors and response factors are a measure of the slope of the calibration relationship and assume that the curve passes through the origin. Under ideal conditions, the factors will not vary with the concentration of the standard that is injected into the instrument. In practice, some variation is to be expected. However, when the variation, measured as the relative standard deviation (RSD), is less than or equal to 20%, the use of the linear model is generally appropriate, and the calibration curve can be assumed to be linear and to pass through the origin.

NOTE: Linearity through zero is a statistical assumption and not a rationale for reporting results below the calibration range demonstrated by the analysis of the standards

To evaluate the linearity of the initial calibration, calculate the mean CF (external standard calibration) or RF (internal standard calibration), the standard deviation (SD), and the RSD as follows:

$$\text{mean CF} = \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n} \qquad \text{mean RF} = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n}$$

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (CF_i - \overline{CF})^2}{n - 1}} \qquad SD = \sqrt{\frac{\sum_{i=1}^{n} (RF_i - \overline{RF})^2}{n - 1}}$$

$$RSD = \frac{SD}{\overline{CF}} \times 100 \qquad RSD = \frac{SD}{\overline{RF}} \times 100$$

where *n* is the number of calibration standards and RSD is expressed as a percentage (%).

If the RSD of the calibration or response factors is less than or equal to 20% over the calibration range, then linearity through the origin may be assumed, and the average calibration or response factor may be used to determine sample concentrations.

7.5.1.1 Given the potentially large numbers of analytes that may be analyzed in some methods, it is likely that some analytes may exceed the 20% acceptance limit for the RSD for a given calibration. In those instances, the following steps are recommended, but not required.

The first step is generally to check the instrument operating conditions. The suggested maintenance procedures in Sec. 7.11 may be useful in guiding such adjustments. This option will apply in those instances where a linear instrument response is expected. It may involve some trade-offs to optimize performance across all target analytes. For instance, changes to the operating conditions necessary to achieve linearity for problem compounds may cause the RSD for other compounds to increase, but as long as all analytes meet the RSD limits for linearity, the calibration is acceptable.

If the RSD for any analyte is greater than 20%, the analyst may wish to review the results (area counts, calibration or response factors, and RSD) for those analytes to ensure that the problem is not associated with just one of the five initial calibration standards. If the problem appears to be associated with a single standard, that one standard may be reanalyzed and the RSD recalculated. Replacing the standard may be necessary in some cases.

A third alternative is to narrow the calibration range by replacing one or more of the calibration standards with standards that cover a narrower range. If linearity can be achieved using a narrower calibration range, document the calibration linearity, and proceed with analyses. The changes to the upper end of the calibration range will affect the need to dilute samples above the range, while changes to the lower end will affect the overall sensitivity of the method. Consider the regulatory limits or action levels associated with the target analytes when adjusting the lower end of the range.

NOTE: As noted in Sec. 7.4.1.2, the method quantitation limit is established by the concentration of the lowest standard analyzed during the initial calibration. Hence, narrowing the calibration range by changing the concentration of the lowest standard will, by definition, change the method quantitation limit. When the purpose of the analysis is to demonstrate compliance with a specific regulatory limit or action level, the analyst must ensure that the method quantitation limit is at least as low as the regulatory limit or action level.

7.5.1.2 In those instances where the RSD for one or more analytes exceeds 20%, the initial calibration may still be acceptable if the following conditions are met:

7.5.1.2.1 The mean of the RSD values for all analytes in the calibration is less than or equal to 20%. The mean RSD is calculated by summing the RSD value for each analyte and dividing by the total number of analytes. If no analyte has an RSD above 20%, then the mean RSD calculation need not be performed.

7.5.1.2.2 The mean RSD criterion applies to all analytes in the standards, regardless of whether or not they are of interest for a specific project. In other words, if the target analyte is part of the calibration standard, its RSD value is included in the evaluation.

7.5.1.2.3 The data user must be provided with either a summary of the initial calibration data or a specific list of those compounds for which the RSD exceeded 20% and the results of the mean RSD calculation.

NOTE: The analyst and the data user must be aware that the use of the approach listed in Sec. 7.5.1.2.1 (i.e., the average of all RSD values ≤ 20%) will lead to greater uncertainty for those analytes for which the RSD is greater than 20%. The analyst and the data user should review the associated quality control results carefully, with particular attention to the matrix spike and laboratory control sample results (see Sec. 8.0), to determine if the calibration linearity poses a significant concern. If this approach is not acceptable for a particular application, then the analyst may need to employ one of the other calibration approaches (see Secs. 7.5.2 to 7.5.4) or adjust the instrument operating conditions and/or the calibration range until the RSD is ≤ 20%.

7.5.1.3 If all of the conditions in Sec. 7.5.1.2 are met, then the average calibration or response factor may be used to determine sample concentrations, as described in Sec. 7.10.

7.5.2 Linear calibration using a least squares regression

If the RSD of the calibration or response factors is greater than 20% over the calibration range, then linearity through the origin cannot be assumed. If this is the case, the analyst may employ a regression equation that does not pass through the origin. This approach may also be employed based on past experience or *a priori* knowledge of the instrument response. Further, at the discretion of the analyst, this approach also may be used for analytes that do meet the RSD limits in Sec. 7.5.1.

This is most easily achieved by performing a linear regression of the instrument response versus the concentration of the standards. Make certain that the instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). This is a statistical requirement and is not simply a graphical convention.

The analyst may also employ a weighted least squares regression if replicate multi-point calibrations have been performed, e.g., three 5-point curves. For all other instances, an appropriate unweighted least squares method should be used. When using a weighted linear least squares regression, the following weighting factor should be used:

$$\frac{1}{SD^2}$$

where SD is the standard deviation of the replicate results at each individual standard concentration.

The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = ax \quad b$$

where:

y = Instrument response (peak area or height)

a = Slope of the line (also called the coefficient of x)
x = Concentration of the calibration standard
b = The intercept

The analyst should not force the line through the origin, but have the intercept calculated from the five data points. Otherwise, the problems noted with the RSD value will occur, i.e., a line through the origin will not meet the QC specifications. In addition, do not include the origin (0,0) as a sixth calibration point. The use of a linear regression may not be used as a rationale for reporting results below the calibration range demonstrated by the analysis of the standards. The regression calculation will generate a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be greater than or equal to 0.99.

In calculating sample concentrations by the external standard method, the regression equation is rearranged to solve for the concentration (x), as shown below.

$$x = \frac{(y \quad b)}{a}$$

When a weighted linear least squares regression is employed, the regression equation becomes:

$$y = \frac{1}{SD^2}(ax \quad b)$$

which may be rearranged to solve for x, the concentration. Using internal standard quantitation, the regression equation is rearranged as shown below:

$$\frac{A_s C_{is}}{A_{is}} = aC_s \quad b$$

where:

A_s = Area (or height) of the peak for the target analyte in the sample
A_{is} = Area (or height) of the peak for the internal standard
C_s = Concentration of the target analyte in the calibration standard
C_{is} = Concentration of the internal standard
a = Slope of the line (also called the coefficient of C_s)
b = The intercept

In calculating sample concentrations by the internal standard method, the regression equation is rearranged to solve for the concentration of the target analyte (C_s), as shown below.

$$C_s = \frac{\left[\frac{A_s C_{is}}{A_{is}} \quad b\right]}{a}$$

7.5.3 Non-linear calibration

In situations where the analyst knows that the instrument response does not follow a linear model over a sufficiently wide working range, or when the other approaches described here have not met the acceptance criteria, a non-linear calibration model may be employed.

NOTE: It is not EPA's intent to allow non-linear calibration to be used to compensate for detector saturation at higher concentrations or to avoid proper instrument maintenance. Thus, non-linear calibration should not be employed for methods or instruments previously shown to exhibit linear calibration for the analytes of interest.

When using a calibration model for quantitation, the curve must be continuous, continuously differentiable and monotonic over the calibration range. The model chosen should have no more than four parameters, i.e., if the model is polynomial, it may be no more than third order, as in the equation:

$$y = ax^3 \quad bx^2 \quad cx \quad d$$

As noted above, the model must be continuous. A curve is continuous when it has consecutive numerical values along the function, whether increasing or decreasing, and without having breaks in the function (i.e., the pen shall never leave the paper from the minimum to the maximum). The model must also be continuously differentiable, such that all derivatives of the function are continuous functions themselves, and monotonic, such that all tangent lines of the derivative to all of the points on the calibration curve have either only positive or negative slopes.

If the model is not a polynomial, it should not include more than four parameters, i.e.,

$$y = f(a,b,c,d,x)$$

where "f" indicates a function with up to four parameters.

In estimating model parameters for the calibration data, the instrumental response (y) must be treated as the dependent variable, and the calibration of the concentration standard (x) must be the independent variable. Do not force the line through the origin; i.e., do not set the intercept as 0, and do not include the origin (0,0) as a calibration point. Model estimates from the regression must be used as calculated, i.e., if the model is a polynomial, the intercept is d and may not be set to 0. Weighting in a calibration model may significantly improve its accuracy.

The statistical considerations in developing a non-linear calibration model require more data than the more traditional linear approaches described above. Whereas SW-846 methods employ five standards for a linear (first order) calibration model, a quadratic (second order) model requires six standards, and a third order polynomial requires seven standards.

Most curve fitting programs will use some form of least squares minimization to adjust the coefficients of the polynomial (a,b,c, and d, above) to obtain the polynomial that best fits the data. The "goodness of fit" of the polynomial equation is evaluated by calculating the weighted coefficient of the determination (COD).

$$COD = \frac{\sum_{i=1}^{n} (y_{obs} - \bar{y})^2 - \left(\frac{n-1}{n-p}\right) \sum_{i=1}^{n} (y_{obs} - Y_i)^2}{\sum_{i=1}^{n} (y_{obs} - \bar{y})^2}$$

where:

y_{obs} = Observed response (area) for each concentration from each initial calibration standard
$\bar{y}$ = Mean observed response from the initial calibration
Y_i = Calculated (or predicted) response at each concentration from the initial calibration(s)
n = Total number of calibration points (i.e., 6 for a quadratic model; 7 for a third order model)
p = Number of adjustable parameters in the polynomial equation (i.e., 3 for a third order; 2 for a second order polynomial)

Under ideal conditions, with a "perfect" fit of the model to the data, the coefficient of the determination will equal 1.0. In order to be an acceptable non-linear calibration, the COD must be greater than or equal to 0.99.

As noted in Sec. 7.5, whichever of these options is employed, a unique analyte or surrogate concentration must fall within the calibration range. Analysts are advised to check both second and third order calibration models to ensure that this holds true (e.g., no parabolas or repeating functions in the calibration range). Samples with concentrations that exceed the calibration range must be diluted to fall within the range.

7.5.4 Data transformations

An understanding of the fundamental behavior of the detector may be used to choose a data transformation that will then allow for a simple calibration model. For example the response of a flame photometric detector in the sulfur mode is known to be proportional to the square of the sulfur concentration. Therefore, using the data system to take the square root of the instrument response before integration or the square root of the peak height allows for a calibration factor approach rather than a polynomial calibration curve. Instrument response may be transformed prior to any calculations (including integration) subject to the following constraints:

7.5.4.1 Any parameters used in the transformation should be fixed for the calibration and all subsequent analyses and verifications until the next calibration.

7.5.4.2 The transformation model chosen should be consistent with the behavior of the instrument and detector. All data transformations must be clearly defined and documented by the analyst and related back to the fundamental behavior of the detector. In other words, this approach may not be used in the absence of specific knowledge about the behavior of the detector, nor as a "shot in the dark" to describe the calibration.

7.5.4.3 No transformations should be performed on areas or other results (e.g., the transformation must be applied to the instrument response itself).

7.5.4.4 When the transformed data are used to develop calibration factors, those factors must meet the acceptance criteria described in Sec. 7.5.1.

7.6 Retention time windows

Retention time windows are crucial to the identification of target compounds. Absolute retention times are used for compound identification in all GC and HPLC methods that do *not* employ internal standard calibration. Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loadings and normal chromatographic variability. The width of the retention time window should be carefully established to minimize the occurrence of both false positive and false negative results. Tight retention time windows may result in false negatives and/or may cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified. Overly wide retention time windows may result in false positive results that cannot be confirmed upon further analysis.

The following subsections describe one approach that may be used to establish retention time windows for GC and HPLC methods. Other approaches may be employed, provided that the analyst can demonstrate that they provide performance appropriate for the intended application.

NOTE: The criteria listed in Sec. 7.6 are provided for GC and HPLC procedures using non-MS or FTIR detection. Identification procedures are different for GC/MS (e.g., Methods 8260 and 8270), HPLC/MS (e.g., Methods 8321 and 8325), and GC/FT-IR (e.g., Method 8410).

7.6.1 Before establishing retention time windows, make sure that the chromatographic system is operating reliably and that the system conditions have been optimized for the target analytes and surrogates in the sample matrix to be analyzed. Make three injections of all single component standard mixtures and multi-component analytes (such as PCBs) over the course of a 72-hour period. Serial injections or injections over a period of less than 72 hours may result in retention time windows that are too tight.

7.6.2 Record the retention time for each single component analyte and surrogate to three decimal places (e.g., 0.007). Calculate the mean and standard deviation of the three absolute retention times for each single component analyte and surrogate. For multi-component analytes, choose three to five major peaks (see the determinative methods for more details) and calculate the mean and standard deviation of those peaks.

7.6.3 If the standard deviation of the retention times for a target compound is 0.000 (i.e., no difference between the absolute retention times), then the laboratory may either collect data from additional injections of standards or use a default standard deviation of 0.01 minutes. (Recording retention times to three decimal places rather than only two should minimize the instances in which the standard deviation is calculated as 0.000).

7.6.4 The width of the retention time window for each analyte, surrogate, and major constituent in multi-component analytes is defined as ± 3 times the standard deviation of the mean absolute retention time established during the 72-hour period. If the default standard deviation in Sec. 7.6.3 is employed, the width of the window will be 0.03 minutes.

7.6.5 Establish the center of the retention time window for each analyte and surrogate by using the absolute retention time for each analyte and surrogate from the calibration verification standard at

the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.

7.6.6 The laboratory must calculate absolute retention time windows for each analyte and surrogate on each chromatographic column and instrument. New retention time windows must be established when a new GC column is installed. The retention time windows should be reported with the analysis results in support of the identifications made.

7.6.7 If the instrument data system is not capable of employing compound-specific retention time windows, then the analyst may choose the widest window and apply it to all compounds. As noted above, other approaches may also be employed, but must be documented by the analyst.

7.6.8 The surrogates are added to each sample, blank, and QC sample and are also contained in each calibration standard. Although the surrogates may be diluted out of certain sample extracts, their retention times in the calibration standards may be useful in tracking retention time shifts. Whenever the observed retention time of a surrogate is outside of the established retention time window, the analyst is advised to determine the cause and correct the problem before continuing analyses.

7.7 Calibration verification

The calibration relationship established during the initial calibration (Sec. 7.5) must be verified at periodic intervals. The process of calibration verification applies to both external standard and internal standard calibration techniques, as well as to linear and non-linear calibration models.

As a general rule, the initial calibration in an SW-846 method must be verified at the beginning of each 12-hour analytical shift during which samples are analyzed. (Some methods may specify more frequent verifications). The 12-hour analytical shift begins with the injection of the calibration verification standard (or the MS tuning standard in MS methods). The shift ends after the completion of the analysis of the last sample or standard that can be injected within 12 hours of the beginning of the shift.

If the response (or calculated concentration) for an analyte is within ±15% of the response obtained during the initial calibration, then the initial calibration is considered still valid, and the analyst may continue to use the CF or RF values from the initial calibration to quantitate sample results. The ±15% criterion may be superseded in certain determinative methods.

Except where the determinative method contains alternative calibration verification criteria, if the response (or calculated concentration) for any analyte varies from the mean response obtained during the initial calibration by more than ±15%, then the initial calibration relationship may no longer be valid.

NOTE: The process of calibration verification is fundamentally different from the approach called "continuing calibration" in some methods from other sources. As described in those methods, the calibration factors or response factors calculated during continuing calibration are used to update the calibration factors or response factors used for sample quantitation. This approach, while employed in other EPA programs, amounts to a daily single-point calibration, and is not appropriate nor permitted in SW-846 chromatographic procedures for trace environmental analyses.

In keeping with the approach described for initial calibration in Sec 7.5, if the average of the responses for all analytes is within 15%, then the calibration has been verified. However, the conditions in Sec. 7.5.1.2

also apply, e.g., the average must include all analytes in the calibration, regardless of whether they are target analytes for a specific project, and the data user must be provided with the calibration verification data or a list of those analytes that exceeded the 15% limit. The effect of using the average of the response for all analytes for calibration verification will be similar to that for the initial calibration -- namely, that the quantitative results for those analytes where the difference is greater than 15% will include a greater uncertainty. The analyst and the data user should review the note in Sec. 7.5.1.2.

If the calibration does not meet the 15% limit (either on the basis of each compound or the average across all compounds), check the instrument operating conditions, and if necessary, restore them to the original settings, and inject another aliquot of the calibration verification standard. If the response for the analyte is still not within ± 15%, then a new initial calibration must be prepared.

7.7.1 Verification of linear calibrations

Calibration verification for linear calibrations involves the calculation of the percent drift or the percent difference of the instrument response between the initial calibration and each subsequent analysis of the verification standard. Use the equations below to calculate % Drift or % Difference, depending on the procedure specified in the determinative method.

$$\%\ \text{Drift} = \frac{\text{Calculated concentration} \quad \text{Theoretical concentration}}{\text{Theoretical concentration}} \times 100$$

where the calculated concentration is determined using the mean calibration factor or response factor from the initial calibration and the theoretical concentration is the concentration at which the standard was prepared.

$$\%\ \text{Difference} = \frac{CF_v \quad \overline{CF}}{\overline{CF}} \times 100 \qquad \text{or} \qquad = \frac{RF_v \quad \overline{RF}}{\overline{RF}} \times 100$$

where CF_v and RF_v are the calibration factor and the response factor (whichever applies) from the analysis of the verification standard, and $\overline{CF}$ and $\overline{RF}$ are the mean calibration factor and mean response factor from the initial calibration. Except where superseded in certain determinative methods, the % difference or % drift calculated for the calibration verification standard must be within ± 15% for each analyte, or averaged across all analytes (see Sec 7.7), before any sample analyses may take place.

7.7.2 Verification of a non-linear calibration

Calibration verification of a non-linear calibration is performed using the percent drift calculation described in Sec. 7.7.1, above. Except where superseded in certain determinative methods, the % drift calculated for the calibration verification standard must be within ± 15% for each analyte, or averaged across all analytes (see Sec 7.7), before any sample analyses may take place. It may also be appropriate to employ two standards at different concentrations to verify the calibration. In this instance, one standard should be near the inflection point in the curve. The choice of specific standards and concentrations is generally a method- or project-specific consideration.

7.7.3 Regardless of whether a linear or non-linear calibration model is used, if either the percent drift or percent difference criterion is not met, then no sample analyses may take place until the calibration has been verified or a new initial calibration is performed that meets the specifications in Sec.

7.5 and those in the determinative method. If the calibration cannot be verified after the analysis of a single verification standard, then adjust the instrument operating conditions and/or perform instrument maintenance (see Sec. 7.11), and analyze another aliquot of the verification standard. If the calibration cannot be verified with the second standard, then a new initial calibration must be performed.

7.7.4 All target analytes and surrogates, including those reported as non-detects, must be included in a periodic calibration for purposes of retention time confirmation and to demonstrate that calibration verification criteria are being met. The frequency of this periodic calibration is project-, method-, and analyte-specific.

7.7.5 Calibration verification may be performed using both high and low concentration standards from time to time. This is particularly true when the ECD or ELCD is used. These detectors drift and are not as stable as FID or FPD, and periodic use of the high and low concentration standards serves as a further check on the initial calibration. The concentrations of these standards should generally reflect those observed in samples.

7.7.6 Additional analyses of the mid-point calibration verification standard during a 12-hour analytical shift are strongly recommended for methods involving external standard calibration. If the response for any analyte varies from the average initial calibration response by more than 15% in these additional determinations, corrective action (see Sec. 7.11) may be necessary to restore the system or a new calibration curve should be prepared for that compound.

The frequency of verification necessary to ensure accurate measurement is dependent on the detector and the sample matrix. Very sensitive detectors that operate in the sub-nanogram range are generally more susceptible to changes in response caused by column contamination and sample carryover. Therefore, more frequent verification of calibration (i.e., after every 10 samples) may be necessary for the electron capture, electrochemical conductivity, photoionization, and fluorescence detectors.

Sec. 8.2.2 specifies that samples analyzed using external standards must be bracketed by periodic analyses of standards that meet the QC acceptance criteria (e.g., calibration and retention time). Therefore, more frequent analyses of standards will minimize the number of sample extracts that would have to be reinjected if the QC limits are violated for the standard analysis. The results from these bracketing standards must meet the calibration verification criteria in Sec. 7.7.1 and 7.7.2 and the retention time criteria in Sec. 7.6. However, if the standard analyzed <u>after</u> a group of samples exhibits a response for an analyte that is <u>above</u> the acceptance limit, i.e., $> 15\%$, and the analyte was <u>not</u> detected in any of the previous samples during the analytical shift, then the sample extracts do not need to be reanalyzed, as the verification standard has demonstrated that the analyte would have been detected were it present.

7.7.7 Any method blanks specified in the preparative methods (Methods 3500 and 3600) may be run immediately after the calibration verification analyses to confirm that laboratory contamination does not cause false positive results, or at any other time during the analytical shift. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples.

7.8 Chromatographic analysis of samples

7.8.1 Introduction of sample extracts into the chromatograph varies, depending on the volatility of the compound. Volatile organics are primarily introduced by purge-and-trap techniques (Method 5030, water and Method 5035, soils). However, the use of Method 5021, or another headspace technique, may be advisable for screening volatiles in some sample matrices to prevent overloading and contamination of the purge-and-trap system. Semivolatile and non-volatile analytes are introduced by direct or split/splitless injection.

7.8.1.1 Manual injection (GC)

Inject 1-5 µL of the sample extract. The use of the solvent flush technique is necessary for packed columns. Use 1-2 µL of sample extract for capillary columns.

7.8.1.2 Automated injection (GC)

Using automated injection, smaller volumes (i.e., 1 µL) may be injected, and the solvent flush technique is not necessary. Laboratories should demonstrate that the injection volume is reproducible.

7.8.1.3 Purge-and-trap

Refer to Methods 5000, 5030, or 5035 for details.

7.8.1.4 Manual injection (HPLC)

Inject 10-100 µL. This is generally accomplished by over-filling the injection loop of a zero-dead-volume injector. Larger volumes may be injected if better sensitivity is required, however, chromatographic performance may be affected.

7.8.1.5 Automated injection (HPLC)

Inject 10-100 µL. Laboratories should demonstrate that the injection volume is reproducible. Larger volumes may be injected if greater sensitivity is required, however, chromatographic performance may be adversely affected.

7.8.2 All analyses, including field samples, matrix spike samples, matrix spike duplicates, laboratory control samples, method blanks, and other QC samples, are performed during an analysis sequence. The sequence begins with instrument calibration, which is followed by the analysis of sample extracts. Verification of calibration and retention times is necessary no less than once every 12-hour analytical shift. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded. As noted in Secs. 7.7.6 and 8.2.2, when employing external standard calibration, it is necessary that a calibration verification standard be run at the end of the sequence to bracket the sample analyses. Acceptance criteria for the initial calibration and calibration verification are described in Secs. 7.5 - 7.7.

Analysis of calibration verification standards every 10 samples is strongly recommended, especially for the highly sensitive GC and HPLC detectors that detect sub-nanogram concentrations. Frequent analysis of calibration verification standards helps ensure that chromatographic systems are performing acceptably and that false positives, false negatives and poor quantitations are minimized. Samples analyzed using external standard calibration must be bracketed by the analyses of calibration

standards that meet the QC limits for verification of calibration and retention times. If criteria are exceeded, corrective action must be taken (see Sec. 7.11) to restore the system and/or a new calibration curve must be prepared for that compound and the samples must be reanalyzed.

Certain methods may also include QC checks on column resolution, analyte degradation, mass calibration, etc., at the beginning of a 12-hour analytical shift.

7.8.3 Sample concentrations are calculated by comparing sample responses with the initial calibration of the system (Sec. 7.5). If sample response exceeds the limits of the initial calibration range, dilute the extract (or sample) and reanalyze. Extracts should be diluted so that all peaks are on scale, as overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, is acceptable, as long as calibration limits are not exceeded. When overlapping peaks cause errors in peak area integration, the use of peak height measurements is recommended.

7.8.4 If chromatographic peaks are masked by the presence of interferences, further sample cleanup is necessary. See Method 3600 for guidance.

7.8.5 When there are a large number of target analytes, it may be difficult to fully resolve these compounds. Examples of chromatograms for the compounds of interest are provided in many determinative methods.

7.9 Compound Identification

Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window. Confirmation is necessary when the composition of samples is not well characterized. Confirmation techniques include analysis on a second column with dissimilar stationary phase, by GC/MS (full scan or SIM) or HPLC/MS (if concentration permits), HPLC/UV data at two different wavelengths, GC or HPLC data from two different detectors, or by other recognized confirmation techniques. For HPLC/UV methods, the ability to generate UV spectra with a diode array detector may provide confirmation data from a single analysis, provided that the laboratory can demonstrate this ability for typical sample extracts (not standards) by comparison to another recognized confirmation technique.

When confirmation is made on a second column, that analysis should meet all of the QC criteria described above for calibration, retention times, etc. Confirmation is not required for GC/MS and HPLC/MS methods.

Confirmation may not be necessary if the composition of the sample matrix is well established by prior analyses, for instance, when a pesticide known to be produced or used in a facility is found in a sample from that facility.

When using GC/MS for confirmation, ensure that GC/MS analysis is performed on an extract at the appropriate pH for the analyte(s) being confirmed, i.e., do not look for basic analytes in an acidic extract. Certain analytes, especially pesticides, may degrade if extraction conditions were either strongly acidic and/or strongly basic.

Many chromatographic interferences result from co-elution of one or more compounds with the analyte of interest, or may be the result of the presence of a non-analyte peak in the retention time window of an analyte. Such co-elution problems affect quantitation as well as identification, and may result in poor agreement between the quantitative results from two dissimilar columns. Therefore, even when the

identification has been confirmed on a dissimilar column, the analyst should evaluate the agreement of the quantitative results on both columns, as described in Sec. 7.10.4.

7.10 Calculations

The calculation of sample results depends on the type of calibration (external or internal standard) and the calibration model employed (linear or non-linear). The following sections describe the calculations used in each instance. Specific determinative methods may contain additional information.

7.10.1 External standard calibration - linear calibration

The concentration of each analyte in the sample is determined by comparing the detector response (peak area or height) to the response for that analyte in the initial calibration. The concentration of an analyte may be calculated as follows, depending on the sample matrix:

7.10.1.1 Aqueous samples

$$\text{Concentration } (\mu g/L) = \frac{(A_s)(V_t)(D)}{(\overline{CF})(V_i)(V_s)}$$

where:

A_s = Area (or height) of the peak for the analyte in the sample.

V_t = Total volume of the concentrated extract (µL). For purge-and-trap analysis, V_t is not applicable and therefore is set at 1.

D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless.

$\overline{CF}$ = Mean calibration factor from the initial calibration (area per ng).

V_i = Volume of the extract injected (µL). The nominal injection volume for samples and calibration standards must be the same. For purge-and-trap analysis, V_i is not applicable and therefore is set at 1. If concentration units are used in calculating the calibration factor (see Sec. 7.4.2.1), then V_i is not used in this equation.

V_s = Volume of the aqueous sample extracted or purged in mL. If units of liters are used for this term, multiply the results by 1000.

Using the units specified here for these terms will result in a concentration in units of ng/mL, which is equivalent to µg/L.

7.10.1.2 Nonaqueous samples

$$\text{Concentration } (\mu g/kg) = \frac{(A_s)(V_t)(D)}{(\overline{CF})(V_i)(W_s)}$$

where A_s, V_t, D, $\overline{CF}$, and V_i are as described in 7.10.1.1, and

W_s = Weight of sample extracted or purged (g). Either the wet weight or dry weight may be used, depending upon the specific application of the data. If units of kilograms are used for this term, multiply the results by 1000.

Using the units specified here for these terms will result in a concentration in units of ng/g, which is equivalent to µg/kg.

For purge-and-trap analyses where a volume of methanol extract is added to organic-free reagent water and purged, V_t is the total volume of the methanol extract and V_i is the volume of methanol extract that is added to the 5 mL of organic-free reagent water.

7.10.1.3 If a linear calibration that does not pass through the origin has been employed, the regression equation is rearranged as shown in Sec.7.5.2, and the concentration of the analyte is calculated from the area response(y), the slope(a) and the intercept(b). When using this form of linear calibration, it is the laboratory's responsibility to ensure that the calculations take into account the volume or weight of the original sample, dilution factor (if any) and dry weight (as applicable). One approach to this calculation is to perform the original linear regression using the concentration of the analyte in the final extract volume or the volume purged. The concentration of the analyte in the sample may then be calculated as follows:

$$C_s = \frac{(C_{ex})(V_t)}{(V_s)}$$

where:

C_s = Concentration in the sample
C_{ex} = Concentration in the final extract
V_t = Total volume of the concentrated extract
V_s = Volume of the sample extracted or purged

For solid samples, substitute the weight of the sample, W_s, for V_s.

For purge-and-trap analyses, the concentration of the analyte in the volume of the sample that is purged will be the same as in the original sample, except when dilutions are performed.

7.10.2 Internal standard calibration - linear calibration

The concentration of each analyte in the sample is calculated using the results of the initial calibration, according to one of the following sections, depending on the sample matrix:

7.10.2.1 Aqueous samples

$$\text{Concentration } (\mu g/L) = \frac{(A_s)(C_{is})(D)(V_i)}{(A_{is})(\overline{RF})(V_s)(1000)}$$

where:

A_s = Area (or height) of the peak for the analyte in the sample.

A_{is} = Area (or height) of the peak for the internal standard.

C_{is} = Concentration of the internal standard in the concentrated sample extract or volume purged in µg/L.

D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless.

V_i = Volume of the extract injected (µL). The nominal injection volume for samples and calibration standards must be the same. For purge-and-trap analysis, V_i is not applicable and is set at 1.

$\overline{RF}$ = Mean response factor from the initial calibration. Unlike calibration factors for external standard calibration, the response factor is dimensionless (see Sec. 7.5).

V_s = Volume of the aqueous sample extracted or purged (mL). If units of liters are used for this term, multiply the results by 1000.

The 1000 in the denominator represents the number of µL in 1 mL. If the injection (V_i) is expressed in mL, then the 1000 may be omitted.

Using the units specified here for these terms will result in a concentration in units of ng/mL, which is equivalent to µg/L.

7.10.2.2 Nonaqueous samples

$$\text{Concentration } (\mu g/kg) = \frac{(A_s)(C_{is})(D)(V_i)}{(A_{is})(\overline{RF})(W_s)(1000)}$$

where: A_s, A_{is}, C_{is}, D, and $\overline{RF}$ are the same as for aqueous samples, and

W_s = Weight of sample extracted (g). Either a dry weight or wet weight may be used, depending upon the specific application of the data. If units of kilograms are used for this term, multiply the results by 1000.

The 1000 in the denominator represents the number of µL in 1 mL. If the injection (V_i) is expressed in mL, then the 1000 may be omitted.

Using the units specified here for these terms will result in a concentration in units of ng/g, which is equivalent to µg/kg.

7.10.2.3 If a linear calibration that does not pass through the origin has been employed, then the regression equation is rearranged in a fashion similar to that described in Sec. 7.10.1.3.

7.10.3 Calculations for a non-linear calibration curve

When a non-linear curve has been employed, the non-linear model is rearranged to solve for the concentration of the analyte in the extract or purge volume, and the extract concentration is converted to a sample concentration in a fashion similar to that described in Sec. 7.10.1.3.

When non-linear calibrations are employed, it is essential that the laboratory clearly document the calculation of analyte concentrations. Example calculations should be reported that clearly indicate how the instrument response (area) was converted into a sample result.

7.10.4 Comparison between results from different columns or detectors

When sample results are confirmed using two dissimilar columns or with two dissimilar detectors, the agreement between the quantitative results should be evaluated after the identification has been confirmed. Calculate the relative percent difference (RPD) between the two results using the formula below.

$$RPD = \frac{| R_1 - R_2 |}{\left(\frac{R_1 + R_2}{2} \right)} \times 100$$

where R_1 and R_2 are the results on the two columns and the vertical bars in the equation above indicate the absolute value of the difference. Therefore, the RPD is always a positive value.

7.10.4.1 If one result is significantly higher (e.g., > 40%), check the chromatograms to see if an obviously overlapping peak is causing an erroneously high result. If no overlapping peaks are noted, examine the baseline parameters established by the instrument data system (or operator) during peak integration.

7.10.4.2 If no anomalies are noted, review the chromatographic conditions. If there is no evidence of chromatographic problems, report the higher result. This approach is conservative relative to protection of the environment. The data user should be advised of the disparity between the results on the two columns.

7.11 Suggested chromatographic system maintenance

Corrective measures may involve any one or more of the following remedial actions. This list is by no means comprehensive and analysts should develop expertise in troubleshooting their specific instruments and analytical procedures. The manufacturers of chromatographic instruments, detectors, columns, and accessories generally provide detailed information regarding the proper operation and limiting factors associated with their products. The importance of reading and reviewing this information cannot be over-emphasized.

7.11.1 Capillary GC columns

Routine maintenance may compel the analyst to clean and deactivate the glass injection port insert or replace it with a fresh insert that has been cleaned and deactivated with dichlorodimethylsilane. Cut off 0.5 - 1.0 m of the injector end of the column using a 90° cut. Place ferrule onto the column before cutting.

Exceptional maintenance may compel the analyst to replace gas traps and backflush the column with solvent according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the column.

7.11.2 Metal (GC) injector body

Turn off the oven and remove the analytical column when the oven has cooled. Remove the glass injection port insert. Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

Place a beaker beneath the injector port inside the GC oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone and then toluene, catching the rinsate in the beaker.

Prepare a solution of deactivating agent (dichlorodimethylsilane) following manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution, serially rinse the injector body with toluene, methanol, acetone, and hexane. Reassemble the injector and replace the GC column.

7.11.3 HPLC columns

Examine the system and check for drips that are indicative of plumbing leaks. Check that tubing connectors are of the shortest possible length to minimize dead volumes and reduce band broadening. Compatible guard columns should be installed to protect analytical columns.

If degradation of resolution or changes in back pressure are observed, the first action should be to replace the guard column if one is installed. Secondly, temporarily reverse the flow through the column to dislodge contamination in the frit with the column disconnected from the detector. If this does not correct the problem, place the analytical column in a vise, remove the inlet compression fitting and examine the column.

Analysts should establish that no void volume has developed, that the column packing has not become contaminated, and that the frit is not clogged. Void volumes can be filled with compatible packing and frits replaced.

Columns must eventually be replaced as the bonding and end-capping groups used to modify the silica are lost with time. Loss of these groups will result in chromatographic tailing and changes in analyte retention times. Retention times may also change because of differences in column temperature or because the composition of the solvent gradient is not completely reproducible.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. The development of in-house QC limits for each method is encouraged, as described in Sec. 8.7. The use of instrument-specific QC limits is encouraged, provided such limits will generate data appropriate for use in the intended application. In general, the following QC requirements pertain to all the determinative methods listed in Sec. 1.1 unless superseded by specific requirements provided in the determinative method.

8.2 Evaluating chromatographic performance

The analyst's expertise in performing chromatography is a critical element in the successful performance of chromatographic methods. Successful generation of data requires selection of suitable preparation and analysis methods and an experienced staff to use these methods.

8.2.1 For each 12-hour period during which analysis is performed, the performance of the entire analytical system should be checked. These checks should be part of a formal quality control program that includes the analysis of blanks, calibration standards, matrix spikes, laboratory control samples and replicate samples, although all of these checks need not be performed during each shift.

8.2.2 Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. Therefore, all sample analyses performed using external standard calibration must be bracketed with acceptable calibration verification standards.

8.2.3 In addition to the quantitative measures of comparison described below and in the individual methods, analysts should evaluate chromatograms and instrument operation. Questions that should be asked include:

Do the peaks look normal (Gaussian)?
Is the response obtained comparable to the response from previous calibrations?
Do the column fittings need tightening?
Are non-target peaks present in calibration analyses?
Are contaminants present in the blanks?
Is the injector leaking (e.g., does the GC injector septum need replacing)?
Does the HPLC guard column need replacement?

8.2.4 Significant peak tailing, leaks, changes in detector response and laboratory contamination should be corrected. Tailing problems are generally traceable to active sites on the column, cold spots in a GC, improper choice of HPLC mobile phase, the detector inlet, or leaks in the system.

8.2.5 Recalibration of the instrument must take place when the performance changes to the point that the calibration verification acceptance criteria (Sec. 7.7) cannot be achieved. In addition, significant maintenance activities or hardware changes may also require recalibration. The sections below provide general guidance on the sorts of procedures that may or may not require recalibration.

8.2.5.1 There are various types of instrument maintenance that should <u>not</u> automatically require recalibration of the instrument. Examples include changing: septa; compressed gas cylinders; syringes; moisture, hydrocarbon, or oxygen traps; solvents in an ELCD; purge tubes; PTFE transfer lines; glow plugs; split seals; column fittings; inlets; or filaments. Other procedures include breaking off or changing a guard column or cleaning the inlet. Whenever such procedures are performed, the analyst must demonstrate that the results for a calibration verification standard meet the acceptance criteria in Sec. 7.7. before the analysis of any samples. Otherwise, recalibration is required.

8.2.5.2 In contrast to Sec. 8.2.5.1, some maintenance procedures are so likely to affect the instrument response that recalibration is <u>automatically</u> required, regardless of the ability to meet the calibration verification acceptance criteria. These procedures include: changing,

replacing, or reversing the column; recoating the bead in a detector; changing nitrogen tubes in an NPD; changing resins; changing the PID seal or lamp; changing the FID jet; changing the entrance lens, draw out lens or repeller; cleaning the MS source; changing the electron multiplier, ion source chamber, or injector port. Whenever such procedures are performed, the analyst must perform a new initial calibration that meets the requirement using Sec 7.5. As noted in Sec. 7.6, changing or replacing the column will also require that the retention time windows be redetermined.

8.2.6 The analysis of method blanks is critical to the provision of meaningful sample results. Consult the appropriate 3500 or 5000 series method for the specifics of the preparation of method blanks. The following general guidelines apply to the interpretation of method blank results.

8.2.6.1 Method blanks should be prepared at a frequency of at least 5%, that is, one method blank for each group of up to 20 samples prepared at the same time, by the same procedures. For samples analyzed for volatiles by the purge-and-trap technique, the preparation is equivalent to the analysis. Therefore, one purge-and-trap method blank must be analyzed with each group of up to 20 samples analyzed on the same instrument during the same analytical shift.

8.2.6.2. When samples that are extracted together are analyzed on separate instruments or on separate analytical shifts, the method blank associated with those samples (e.g., extracted with the samples) must be analyzed on at least one of those instruments. A solvent blank should be analyzed on all other instruments on which the set of samples were analyzed to demonstrate that the instrument is not contributing contaminants to the samples.

8.2.6.3 Unless otherwise described in a determinative method, the method blank may be analyzed immediately after the calibration verification standard, to ensure that there is no carryover from the standard, or at another point in the analytical shift.

8.2.6.4 When sample extracts are subjected to cleanup procedures, the associated method blank must also be subjected to the same cleanup procedures.

8.2.6.5 As described in Chapter One, the results of the method blank should be:

8.2.6.5.1 Less than the laboratory's MDL for the analyte or less than the level of acceptable blank contamination specified in the approved quality assurance project plan.

8.2.6.5.2 Less than 5% of the regulatory limit associated with an analyte.

8.2.6.5.3 Or less than 5% of the sample result for the same analyte, whichever is greater.

8.2.6.5.4 If the method blank results do not meet the acceptance criteria above, then the laboratory should take corrective action to locate and reduce the source of the contamination and to re-extract and reanalyze any samples associated with the contaminated method blank.

8.2.6.6 The laboratory should <u>not</u> subtract the results of the method blank from those of any associated samples. Such "blank subtraction" is inappropriate for the GC and

HPLC methods addressed here, and often leads to negative sample results. If the method blank results do not meet the acceptance criteria in 8.2.6.5 and reanalysis is not practical, then the data user should be provided with the sample results, the method blank results, and a discussion of the corrective actions undertaken by the laboratory.

8.2.6.7 Method blanks and/or solvent blanks may also be used to check for contamination by carryover from a high-concentration sample into subsequent samples (see Sec. 3.1). When the analysis of such blanks is not possible, such as when an unattended autosampler is employed, the analyst should review the results for at least the next two samples after the high-concentration sample. If analytes in the high-concentration sample are not present in the subsequent samples, then the lack of carryover has been demonstrated. If there is evidence that carryover may have occurred, then the samples should be reanalyzed.

8.3 Summary of required instrument QC

The following criteria primarily pertain to GC and HPLC methods with non-MS or FTIR detectors, and may be superseded by criteria specified in individual determinative methods (e.g., Methods 8021, 8260, 8270, 8321, 8325, and 8410).

8.3.1 The criteria for linearity of the initial calibration curve is an RSD of $\leq$ 20%.

8.3.2 For non-linear calibration curves, the coefficient of the determination (COD) must be greater than or equal to 0.99 (see Sec. 7.5.2).

8.3.3 Retention time (RT) windows must be established for the identification of target analytes. See Sec. 7.6 for guidance on establishing the absolute RT windows.

8.3.4 The retention times of all analytes in all verification standards must fall within the absolute RT windows. If an analyte falls outside the RT window in a calibration verification standard, new absolute RT windows must be calculated, unless instrument maintenance corrects the problem.

8.3.5 The calibration verification results must be within $\pm$ 15% of the response calculated using the initial calibration. If the limit is exceeded, a new standard curve must be prepared unless instrument maintenance corrects the problem.

8.4 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with each combination of sample preparation and determinative methods that it utilizes, by generating data of acceptable accuracy and precision for a reference sample containing the target analytes in a clean matrix. The laboratory must also repeat this demonstration whenever new staff are trained or significant changes in instrumentation are made.

8.4.1 The reference samples are prepared from a spiking solution containing each analyte of interest. The reference sample concentrate (spiking solution) may be prepared from pure standard materials, or purchased as certified solutions. If prepared by the laboratory, the reference sample concentrate must be made using stock standards prepared independently from those used for calibration.

Preparation of the reference sample concentrate is dependent upon the method being evaluated.

Guidance for reference sample concentrations for certain methods are listed in Sec. 8.0 of Methods 3500 and 5000. In other cases, the determinative methods contain guidance on preparing the reference sample concentrate and the reference sample. If no guidance is provided, prepare a reference sample concentrate in methanol (or any water miscible solvent) at a concentration such that the spike will provide a concentration in the clean matrix that is 10 - 50 times the MDL for each analyte in that matrix.

The concentration of target analytes in the reference sample may be adjusted to more accurately reflect the concentrations that will be analyzed by the laboratory. If the concentration of an analyte is being evaluated relative to a regulatory limit or action level, see Sec. 8.5.1 for information on selecting an appropriate spiking level.

8.4.2 To evaluate the performance of the total analytical process, the reference samples must be handled in exactly the same manner as actual samples. Use a clean matrix for spiking purposes (one that does not have any target or interference compounds), e.g., organic-free reagent water for the aqueous matrix and organic-free sand or soil for the solid matrix.

8.4.3 Preparation of reference samples

8.4.3.1 Volatile organic analytes

Prepare the reference sample by adding 200 µL of the reference sample concentrate (Sec. 8.4.1) to 100 mL of organic-free reagent water. Transfer this solution immediately to a 20- or 25-mL (or four 5-mL) gas-tight syringe(s) when validating water analysis performance by Method 5030. Alternatively, the reference sample concentrate may be injected directly through the barrel of the 5- or 25-mL syringe. See Method 5000 (Sec. 8.0) for guidance on other preparative methods and matrices.

8.4.3.2 Semivolatile and nonvolatile organic analytes

Prepare the reference sample by adding 1.0 mL of the reference sample concentrate (Sec. 8.4.1) to each of four 1-L aliquots of organic-free reagent water. See Method 3500 (Sec. 8.0) for other matrices.

8.4.4 Analyze at least four replicate aliquots of the well-mixed reference samples by the same procedures used to analyze actual samples (Sec. 7.0 of each of the methods). This will include a combination of the sample preparation method (usually a 3500 series method for extractable organics or a 5000 series method for volatile organics) and the determinative method (an 8000 series method).

8.4.5 Calculate the average recovery ($\bar{x}$) in µg/L, and the standard deviation of the recovery (s) in µg/L, for each analyte of interest using the four results.

8.4.6 Multiple-laboratory performance data are included in some determinative methods and may be used as guidance in evaluating performance in a single laboratory. Compare s and $\bar{x}$ for each analyte with the corresponding performance data for precision and accuracy given in the performance data table at the end of the determinative method. If s and $\bar{x}$ for all analytes of interest meet the appropriate acceptance criteria, then the system performance is acceptable and analysis of actual samples can begin. If any individual s value exceeds the precision limit or any individual $\bar{x}$ value falls outside the range for accuracy, then the system performance may be unacceptable for that analyte.

NOTE: The large number of analytes in each of the methods presents a substantial probability that one or more analyte will fail at least one of the performance criteria when all analytes of a given method are determined.

When one or more of the analytes fail at least one of the performance criteria, the analyst should proceed according to Sec. 8.4.6.1 or 8.4.6.2.

8.4.6.1 Locate and correct the source of the problem and repeat the test for all analytes of interest, beginning at Sec. 8.4.2.

8.4.6.2 Beginning at Sec. 8.4.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning at Sec. 8.4.2.

8.4.7 The performance data in many of the methods are based on single-laboratory performance. As with the multiple-laboratory data, the criteria in those methods may be used as guidance when evaluating laboratory performance. When comparing your laboratory data to performance data developed from single-laboratory data, certain analytes may be outside the limits, however, the majority should be within the acceptance limits.

8.4.8 Even when the determinative method contains performance data (either multiple-laboratory or single-laboratory), the development of in-house acceptance limits is strongly recommended, and may be accomplished using the general considerations described in Sec. 8.7.

8.4.9 In the absence of recommended acceptance criteria for the initial demonstration of proficiency, the laboratory should use recoveries of 70 - 130% as guidance in evaluating the results. Given that the initial demonstration is performed in a clean matrix, the average recoveries of analyte from the four replicates should generally fall within this range. In addition, since the laboratory will repeat the initial demonstration of proficiency whenever new staff are trained or significant changes in instrumentation are made, the resulting data should be used to develop in-house acceptance criteria, as described in Sec. 8.7.

8.5 Matrix spike and laboratory control samples

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this will include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate (MS/MSD) pair with each batch of up to 20 samples of the same matrix processed together (see Chapter One). If samples are expected to contain the target analytes of concern, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample as an alternative to the MS/MSD pair (see Sec. 8.5.3).

In the case of purge-and-trap methods, the MS/MSD, or MS and duplicate samples, should be prepared and analyzed concurrently with the samples. In the case of samples that involve an extraction procedure, the MS/MSD, or MS and duplicate samples, should be extracted with the batch of samples but may be analyzed at any time.

In addition, a Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or

volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicates a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

The concentration of the matrix spike sample and/or the LCS should be determined as described in Secs. 8.5.1 and 8.5.2.

8.5.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit or action level, the spike should be at or below the limit, or 1 - 5 times the background concentration (if historical data are available), whichever concentration is higher.

If historical data are not available, it is suggested that a background sample of the same matrix from the site be submitted for matrix spiking purposes to ensure that high concentrations of target analytes and/or interferences will not prevent calculation of recoveries.

8.5.2 If the concentration of a specific analyte in a sample is not being checked against a limit specific to that analyte, then the analyst may spike the sample at the same concentration as the reference sample (Sec. 8.4.1), at 20 times the estimated quantitation limit (EQL) in the matrix of interest, or at a concentration near the middle of the calibration range. It is again suggested that a background sample of the same matrix from the site be submitted as a sample for matrix spiking purposes.

8.5.3 To develop precision and accuracy data for each of the spiked compounds, the analyst has two choices: analyze the original sample, and an MS/MSD pair; or analyze the original sample, a duplicate sample, and one spiked sample. If samples are not expected to contain the target analytes of concern, then the laboratory may use a matrix spike and matrix spike duplicate pair. If samples are expected to contain the target analytes of concern, then the laboratory may use one matrix spike and a duplicate analysis of an unspiked field sample as an alternative to the MS/MSD pair.

Begin by analyzing one sample aliquot to determine the background concentration of each analyte. Prepare a matrix spike concentrate according to one of the options specified in Sec. 8.5.1 or 8.5.2.

Prepare a matrix spike sample by adding the appropriate volume of the matrix spike concentrate to another aliquot of the sample to yield the desired concentration (see Secs. 8.5.1 and 8.5.2). Prepare a matrix spike duplicate sample from a third aliquot of the sample.

Analyze the MS/MSD samples using the same procedures employed for the original sample, and calculate the concentration of each analyte in the matrix spike and matrix spike duplicate. Likewise, analyze the LCS samples using the same procedures employed for the original sample, and calculate the concentration of each analyte in the LCS.

8.5.3.1 Calculation of recovery

Accuracy is estimated from the recovery of spiked analytes from the matrix of interest. Laboratory performance in a clean matrix is estimated from the recovery of analytes in the LCS. Calculate the recovery of each spiked analyte in the matrix spike, matrix spike duplicate (if performed) and LCS according to the following formula.

$$\text{Recovery} = \%R = \frac{C_s - C_u}{C_n} \times 100$$

where:

C_s = Measured concentration of the spiked sample aliquot
C_u = Measured concentration of the unspiked sample aliquot (use 0 for the LCS)
C_n = Nominal (theoretical) concentration increase that results from spiking the sample, or the nominal concentration of the spiked aliquot (for LCS)

8.5.3.2 Calculation of precision

Precision is estimated from the relative percent difference (RPD) of the concentrations (*not* the recoveries) measured for matrix spike/matrix spike duplicate pairs, or for duplicate analyses of unspiked samples. Calculate the RPD according to the formula below.

$$\text{RPD} = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where:

C_1 = Measured concentration of the first sample aliquot
C_2 = Measured concentration of the second sample aliquot

8.5.4 Recommended QC acceptance criteria for matrix spike samples and LCS

It is necessary for the laboratory to develop single-laboratory performance data for accuracy and precision in the matrices of interest (see Sec. 8.7). In addition, laboratories should monitor method performance in each matrix, through the use of control charts and other techniques.

Many methods may not contain recommended acceptance criteria for LCS results. The laboratory should use 70 - 130% as interim acceptance criteria for recoveries of spiked analytes, until in-house LCS limits are developed (see Sec. 8.7). Where in-house limits have been developed for matrix spike recoveries, the LCS results should fall within those limits, as the LCS is prepared in a clean matrix.

Even where the determinative methods provide performance criteria for matrix spikes and LCS, it is necessary for laboratories to develop in-house performance criteria and compare them to those in the methods. The development of in-house performance criteria is discussed in Sec. 8.7.

As a general rule, the recoveries of most compounds spiked into samples should fall within the range of 70 - 130%, and this range should be used as a guide in evaluating in-house performance. However, as described in Sec. 8.5.4.1, matrix spike recoveries and LCS recoveries may be affected by the spike-to-background ratio.

Where methods do contain performance data for the matrix of interest, use Secs. 8.5.4.1 and 8.5.4.2 as guidance in evaluating data generated by the laboratory.

8.5.4.1 When multiple-laboratory performance data for the matrix of interest are provided in the determinative method, compare the percent recovery (%R) for each analyte in a water sample with the performance data. Given that such performance criteria were developed from multi-laboratory data, they should be met in almost all laboratories. See Sec. 8.7.10 for more information on comparisons between limits. The performance data include an allowance for error in measurement of both the background and spike concentrations, and assume a spike-to-background ratio of 5:1. If spiking was performed at a concentration lower than that used for the reference sample (Sec. 8.4), the analyst may use either the performance data presented in the tables, or laboratory-generated QC acceptance criteria calculated for the specific spike concentration, provided that they meet the project-specific data quality objectives.

8.5.4.2 When the sample was spiked at a spike-to-background ratio other than 5:1, the laboratory should calculate acceptance criteria for the recovery of an analyte. Some determinative methods contain a table entitled "Method Accuracy and Precision as a Function of Concentration" which gives equations for calculating accuracy and precision as a function of the spiking concentration. These equations may be used as guidance in establishing the acceptance criteria for matrix spike samples.

The equations are the result of linear regression analyses of the performance data from a multiple-laboratory study. The equations are of the form:

$$\text{Accuracy} = x = (a)C + b$$

where a is a number less than 1.0, b is a value greater than 0.0, and C is the test concentration (or true value).

Performance criteria for accuracy may be calculated from these equations by substituting the spiking concentration used by the laboratory in place of "C," and using the values of a and b given in the table for each analyte.

Performance criteria for precision are calculated in a similar fashion, using the a and b values for precision given in the table for each analyte. Precision may be calculated as single analyst precision, or overall precision, using the appropriate equations from the table. An acceptable performance range may be calculated for each analyte as:

$$\text{Acceptance range } (\mu g/L) = \text{Accuracy} \pm (2.44)\text{Precision}$$

8.5.5 Also compare the recovery data from the matrix spike with the LCS data (use the average recovery if a matrix spike and matrix spike duplicate were analyzed). If any individual percent recovery in the matrix spike (or matrix spike duplicate) falls outside the designated range for recovery, the laboratory should determine if there is a matrix effect or a laboratory performance problem. A matrix effect is indicated if the LCS data are within limits but the matrix spike data exceed the limits. The surrogate recovery data (Sec. 8.6) should also be used to evaluate the data. Recoveries of both matrix spike compounds and surrogates that are outside of the acceptance limits suggest more pervasive analytical problems then problems with the recoveries of either matrix spikes or surrogates alone.

8.6 Surrogate recoveries

8.6.1 It is necessary that the laboratory evaluate surrogate recovery data from individual samples versus surrogate recovery limits developed in the laboratory. The general considerations for developing in-house acceptance criteria for surrogate recoveries are described in Sec. 8.7.

8.6.2 Surrogate recovery is calculated as:

$$\text{Recovery (\%)} = \frac{\text{Concentration (or amount) found}}{\text{Concentration (or amount) added}} \times 100$$

If recovery is not within in-house surrogate recovery limits, the following procedures are necessary.

8.6.2.1 Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly. Examine chromatograms for interfering peaks and integrated peak areas.

8.6.2.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract (or re-analyze the sample for volatiles).

8.6.2.3 Some samples may require dilution in order to bring one or more target analytes within the calibration range or to overcome significant interferences with some analytes. This may result in the dilution of the surrogate responses to the point that the recoveries can not be measured. If the surrogate recoveries are available from a less-diluted or undiluted aliquot of the sample or sample extract, those recoveries may be used to demonstrate that the surrogates were within the QC limits, and no further action is required. However, the results of both the diluted and undiluted (or less-diluted) analyses should be provided to the data user.

8.6.2.4 If no instrument problem is found, the sample should be re-extracted and re-analyzed (or re-analyze the sample for volatiles).

8.6.2.5 If, upon re-analysis (in either 8.6.2.2 or 8.6.2.4), the recovery is again not within limits, report the data as an "estimated concentration." If the recovery is within the limits in the re-analysis, provide the re-analysis data to the data user. If the holding time for the method has expired prior to the re-analysis, provide both the original and re-analysis results to the data user, and note the holding time problem.

8.7 Generating performance criteria for matrix spike recoveries, surrogate recoveries, initial demonstration of proficiency, and laboratory control sample recoveries

It is essential that laboratories calculate in-house performance criteria for matrix spike recoveries and surrogate recoveries. It may also be useful to calculate such in-house criteria for laboratory control sample (LCS) recoveries and for the initial demonstration of proficiency when experience indicates that the criteria recommended in specific methods are frequently missed for some analytes or matrices. The development of in-house performance criteria and the use of control charts or similar procedures to track laboratory performance cannot be over-emphasized. Many data systems and commercially-available software packages support the use of control charts.

The procedures for the calculation of in-house performance criteria for matrix spike recovery and surrogate recovery are provided below. These procedures may also be applied to the development of in-house criteria for the initial demonstration of proficiency and for LCS recoveries.

8.7.1 For each matrix spike sample analyzed, calculate the percent recovery of each matrix spike compound added to the sample, in a fashion similar to that described in Sec. 8.5.3.3. For each field sample, calculate the percent recovery of each surrogate as described in Sec. 8.6.

8.7.2 Calculate the average percent recovery (p) and the standard deviation (s) for each of the matrix spike compounds after analysis of 15-20 matrix spike samples of the same matrix, using the equations in Sec. 7.5.1, as guidance. Calculate the average percent recovery (p) and the standard deviation (s) for each of the surrogates after analysis of 15-20 field samples of the same matrix, in a similar fashion.

8.7.3 After the analysis of 15-20 matrix spike samples of a particular matrix (or matrix spike limits) or 15-20 field samples (for surrogate limits), calculate upper and lower control limit for each matrix spike or surrogate compound:

Upper control limit = p + 3s
Lower control limit = p - 3s

Calculate warning limits as:

Upper warning limit = p + 2s
Lower warning limit = p - 2s

For laboratories employing statistical software to determine these limits, the control limits approximate a 99% confidence interval around the mean recovery, while the warning limits approximate a 95% confidence interval.

8.7.4 Any matrix spike, surrogate, or LCS results outside of the control limits require evaluation by the laboratory. Such actions should begin with a comparison of the results from the samples or matrix spike samples with the LCS results. If the recoveries of the analytes in the LCS are outside of the control limits, then the problem may lie with the application of the extraction and/or cleanup procedures applied to the sample matrix or with the chromatographic procedures. Once the problem has been identified and addressed, corrective action may include the reanalysis of samples, or the extraction and analysis of new sample aliquots, including new matrix spike samples and LCS.

When the LCS results are within the control limits, the problem may either be related to the specific sample matrix or to an inappropriate choice of extraction, cleanup, and determinative methods. If the results are to be used for regulatory compliance monitoring, then the analyst must take steps to demonstrate that the analytes of concern can be determined in the sample matrix at the levels of interest.

The laboratory may use the warning limits to guide internal evaluations of method performance, track the performance of individual analysts, and monitor the effects of changes to the analytical procedures. Repeated results outside of the warning limits should lead to further evaluation.

8.7.5 Once established, control limits and warning limits for matrix spike compounds should be reviewed after every 10-20 matrix spike samples of the same matrix, and updated at least semi-

annually. Control limits and warning limits for surrogates should be reviewed after every 20-30 field samples of the same matrix, and should be updated at least semi-annually. The laboratory should track trends in both performance and in the control limits themselves. The control and warning limits used to evaluate the sample results should be those in place at the time that the sample was analyzed. Once limits are updated, those limits should apply to all subsequent analyses of new samples.

8.7.6 For methods and matrices with very limited data (e.g., unusual matrices not analyzed often), interim limits should be established using available data or by analogy to similar methods or matrices.

8.7.7 Results used to develop acceptance criteria should meet all other QC criteria associated with the determinative method. For instance, matrix spike recoveries from a GC/MS procedure should be generated from samples analyzed after a valid GC/MS tune and a valid initial calibration that includes the matrix spike compounds. Another example is that analytes in GC or HPLC methods must fall within the established retention time windows in order to be used to develop acceptance criteria.

8.7.8 Laboratories are advised to consider the effects of the spiking concentration on matrix spike performance criteria, and to avoid censoring of data. As noted in Sec. 8.5.4, the acceptance criteria for matrix spike recovery and precision are often a function of the spike concentration used. Therefore, use caution when pooling matrix spike/matrix spike duplicate data for use in establishing acceptance criteria. Not only should the results all be from the same (or very similar) matrix, but the spiking levels should also be approximately the same (within a factor of 2).

Similarly, the matrix spike and surrogate results should all be generated using the same set of extraction, cleanup, and analysis techniques. For example, do not mix results from solid samples extracted by ultrasonic extraction with those extracted by Soxhlet.

8.7.9 Another common error in developing acceptance criteria is to discard data that do not meet a preconceived notion of acceptable performance. This results in a censored data set, which, when used to develop acceptance criteria, will lead to unrealistically narrow criteria. Remember that for a 95% confidence interval, 1 out of every 20 observations likely will still fall outside the limits.

While professional judgement is important in evaluating data to be used to develop acceptance criteria, do not discard specific results simply because they do not meet one's expectations. Rather, employ a statistical test for outlier values, or at least calculate the acceptance limits both with and without the results that are considered suspect and observe the effect of deleting suspect data.

8.7.10 In-house QC limits must be examined for reasonableness. It is not EPA's intent to legitimize poor recoveries that are due to the incorrect choice of methods or spiking levels. In-house limits also should be compared with the objectives of specific analyses. For example, recovery limits (for surrogates, MS, MSD, LCS etc.) that include allowance for a relatively high positive bias (e.g., 70 - 170%) may be appropriate for determining that an analyte is <u>not</u> present in a sample. However, they would be less appropriate for the analysis of samples near but below a regulatory limit, because of the potential high bias.

It may be useful to compare QC limits generated in the laboratory to the performance data that may be listed in specific determinative methods. However, the analyst must be aware that performance data generated from multiple-laboratory data tend to be significantly wider than those generated from single-laboratory data. In addition, comparisons between in-house limits and those from other sources

should generally focus more on the accuracy (recovery) limits of single analyses rather than the precision limits. For example, a mean recovery closer to 100% is generally preferred, even if the ±3 standard deviation range is slightly wider, because those limits indicate that the result is likely closer to the "true value." In contrast, the precision range provides an indication of the results that might be expected from repeated analyses of the same sample.

8.8 It is recommended that the laboratory adopt additional quality assurance practices for use with these methods. The specific practices that are most productive depend upon the needs of the laboratory, the nature of the samples, and project-specific requirements. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer (selected ion monitoring or full scan) must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in the SW-846 analytical methods generally were obtained using organic-free reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects. See Chapter One for more guidance on determination of laboratory-specific MDLs.

9.2 Refer to the determinative methods for method performance information.

10.0 REFERENCES

For further information regarding these methods, review Methods 3500, 3600, 5000, and Chapter One.

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APPENDIX II

REPORTING and DELIVERABLES

Quality Assurance/Quality Control Documentation Required

APPENDIX II
Reporting and Deliverables

QUALITY ASSURANCE/QUALITY CONTROL DOCUMENTATION REQUIRED

The following documentation should be submitted with all analytical data reported. This is applicable to all sample matrices and all types of analysis.

Plans Related to Sampling and Analysis:

One copy of all project plans addressing the sampling and analysis activities should be supplied. Examples of applicable documents might include the following:

- Quality Assurance Project Plan (QAPP)
- Sampling and Analysis Plan (SAP
- Site Assessment Plan
- Closure Plan
- RFI Work Plan
- Voluntary Remediation Work Plan

Sampling Quality Control Data and Information:

- Chain-of-Custody
- Date and time each sample was taken
- Map or diagram indicating sample locations
- Field measurements made (and results)
- Any notable observations *(color, clarity, texture, reaction with preservatives, etc.)*
- Trip blank (or field blank)
- Equipment blank (rinsate blank)
- Identity of field duplicates (a minimum of one duplicate for every 20 or fewer samples)

Laboratory Quality Control Data and Information:

- Completed Chain-of-Custody
- Date and time of receipt at the laboratory
- Condition of samples upon receipt at the laboratory
  E.g.: Temperature of cooler (thermometer reading or presence of ice); condition of bottles (cracked? broken? leaking?); condition of samples (pH reading; preserved? air bubbles present?).
- Facility sample identification or number *(e.g., well no.)*
- Laboratory sample numbers corresponding to facility sample identification
- Sample preparation, extraction, cleanup, or digestion method(s) and date(s)
- Analytical method (name, number, and source) and date of analysis
- Final analytical results
- Case narrative:
  To include deviations from standard analytical or preparatory procedure(s); quality control problems encountered--whether stemming from system, instrumentation, analyst error, or sample matrix; corrective measures taken; if corrective measures as called for in the method were not taken; results of corrective measures taken; etc.

The laboratory documentation listed on the following pages should be provided according to the analytical method(s) used *in addition* to the ***Sampling*** and ***Laboratory Quality Control Data and Information*** listed above. All information pertaining to the method used should be submitted. It may be necessary to explicitly request that the laboratory provide this documentation.

Metals and General Inorganic Analyses

TOTAL AND DISSOLVED METALS by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP) or Atomic Absorption Spectroscopy (AA) and GENERAL INORGANIC ANALYSES

- **!** Method/sample quantitation limits
- **!** Instrument detection limits
- **!** Calibration records and results:
  *Initial calibration:
  --- Calibration curve established for each metal
    - **ICP:** A blank plus at least one calibration standard (containing all target analytes) with a minimum of two replicate exposures
    - **AA:** (graphite furnace and flame emission) A blank plus at least three standards
    - **CVAA:** (mercury by cold vapor AA) A blank plus at least five standards
    - **General Inorganic Analysis:** A blank plus at least three standards
      Additional requirement for cyanide analyses: a mid-range standard must be distilled and analyzed with results compared to curve for undistilled standards.
    - Correlation coefficient of at least 0.995 for each curve (or calibration is repeated)
    - Concentrations and responses for each standard and blank (numeric)
    - Graphical plot of calibration curve (AA analysis)

  --- Date and time of initial calibration
  If not the same day as analysis, provide explanation. If this is allowed by analytical method, cite section of method.
  * Initial and continuing calibration verification (ICV and CCV) (mid-level standard results and % recovery; CCV to be run every ten samples)
- **!** Blank results
  --- Initial and continuing calibration blank results
  --- Method (preparation) blank results
- **!** Matrix spike (sample number of sample spiked, sample concentration for analyte, concentration of spike added, results and % Recovery)
- **!** Matrix spike duplicate or laboratory duplicate (results and Relative Percent Difference [RPD]; if matrix spike duplicate, also report %Recovery)
- **!** Laboratory control sample (QC standard or lab-fortified blank: results and %Recovery)
- **!** Additional deliverables for ICP analysis:
  --- Interference check sample (results and % recovery)
  --- Serial dilution results (five-fold analysis)
  --- ICP Linear Range
  --- Interelement correction factors
- **!** Additional deliverables for AA analysis if Method of Standard Addition (MSA) is used: data and results for MSA
- **!** **Raw data**: To include instrument numerical printouts, instrument peak printouts (all AA and general inorganic, where applicable), lab worksheets, strip chart recordings, sample preparation records, and record of dilutions.

Organic Analyses

VOLATILE ORGANIC ANALYSIS (VOA) and SEMIVOLATILE ORGANIC ANALYSIS (SVOA)
BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

- **!** Tuning criteria and results for:
  ---VOA: Bromofluorobenzene (BFB) or
  ---SVOA: Decafluorotriphenylphosphine (DFTPP)
- **!** Initial calibration data and results:
  --- Calibration standards containing all target analytes run at five concentrations
  --- Retention time (RT) for each target compound in the calibration standards
  --- Response factors (RFs) for each target compound in the calibration standards
  --- Average RF for each compound
  --- Percent relative standard deviation (RSD) for the RFs for the five concentrations of each calibration standard
  --- Date and time of injection
  --- Total ion chromatogram
- **!** Initial and Continuing Calibration Verification data and results (beginning of run and every twelve hours:
  --- RF for each compound in the 50 ppb standard
  --- Percent Difference for RF in 12-hour standard as compared to average RF from initial calibration for each compound
  --- Date and time of injection
- **!** Method blank summary sheet with results, including detections
- **!** Detection/quantitation limit for each compound
- **!** Internal standards summary documented by:
  --- area of primary peak and respective RT for each standard from the 12-hour standard
  --- area of primary peak and respective RT for each standard from each sample
  --- upper and lower acceptance limits clearly defined
- **!** Surrogate (System Monitoring Compound) results (concentration of surrogate spikes added, measured concentrations, and % Recoveries of all surrogates) for each sample
- **!** Matrix Spike/Matrix Spike Duplicate (MS/MSD) results (sample concentration for analyte, concentration of spike added, results, % Recovery for each compound, and Relative Percent Difference between MS and MSD for each compound)
- **!** **Raw Data** for each sample, field duplicate, blank, matrix spike, and matrix spike duplicate including:
  --- total ion chromatogram (indicating surrogates, internal standards, and target compounds detected)
  --- individual mass spectra for target analytes or tentatively identified compounds (TICs, other non-target analytes) detected in each sample and blank (and reference/library search spectra detected analytes or TICs are compared to)
  --- quantitation reports (to include identification of internal and surrogate standards, scan number, area, retention time, concentration of target analytes detected, dilution factors, and date and time of injection).

ANALYSIS OF VOLATILE ORGANIC COMPOUNDS and SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY (GC) Using Method-Specified Detectors (FID, PID, HECD, etc.)

- **!** Initial Calibration, data and results documented by:
  Either an external standard calibration procedure or an internal standard calibration procedure may be used. Calibration factors (CFs) as defined in SW-846 Method 8000A (July 1992) may be reported in place of response factors.
  - --- Calibration standards containing all target analytes run at five concentrations
  - --- Calibration chromatograms
  - --- Response factors (RFs) or CFs or for each target compound in the calibration standards
  - --- Average RF (or average CF) for each compound
  - --- Percent relative standard deviation (%RSD) for the RFs (or CFs) for the five concentrations of each calibration standard
  - --- Date and time of injection (or introduction by purge-and-trap)
- **!** Retention Time (RT) Summary to include:
  - --- RT measured for each target compound from three separate injections over a 72-hour period
  - --- Mean and standard deviations of the three RTs measured (over the 72-hour period)
  - --- RT window for each target compound (mean ± three standard deviations)
  - --- Date and time of injections (or introduction by purge-and-trap)
- **!** Initial and Continuing Calibration Verification (ICV and CCV) documented by:
  Note*: An instrument blank, a QC reference sample ("check sample"), and a midrange calibration standard should be injected at the beginning and end of the run and at intervals in between (at least 1 per 20 samples or 1 per batch if batch is less than 20 samples. 1 per 10 samples is preferred.)*
  - --- Chromatograms for midpoint standard and blank
  - --- RT for each analyte (or major peak(s) of each multicomponent analyte, if applicable) in the midrange standard and comparison to daily RT window
  - --- Percent Difference (%D) between calculated concentration and nominal ("true") concentration of each target analyte in the QC reference sample
  - --- %D between RF or CF of each single component analyte and major peak(s) of each multicomponent analyte in the midrange standard
- **!** Method of sample introduction (direct injection or purge-and-trap)
- **!** Detection/quantitation limit for each compound
- **!** Method blank summary and chromatograms
- **!** Surrogate recoveries for samples, blanks, and spikes
- **!** Matrix spike/matrix spike duplicate (MS/MSD) analysis (minimum of 1 per 20 samples or 1 per batch of less than 20 samples for each matrix)
  OR For medium to high concentration soil and waste samples, laboratory duplicates may be substituted for the MS/MSD.
- **!** **Raw Data** for each sample, standard, field duplicate, blank, matrix spike, and matrix spike duplicate, including dilutions made, chromatograms and preparatory records.
- **!** Confirmation by GC/MS or on second GC column, if required by determinative method or if interference is suspected. Include results and raw data.

QUALITY ASSURANCE/QUALITY CONTROL INFORMATION FOR ANALYSIS OF PESTICIDES and PCBs by Gas Chromatography (GC) with Electron Capture Detector (ECD) or Electrolytic Conductivity Detector (ELCD or HECD)

! Initial Calibration (Include listing of calibration sequence)
An external standard calibration procedure is preferred, but an internal standard procedure may be substituted. If internal standard procedure is used, report Response Factors (RFs) for each compound at each calibration standard concentration, mean RF, and RF %RSD instead of Calibration Factors (CFs).

*For Single Component Analytes, initial calibration is documented by:
--- Five-point calibration preferred; minimum of three-point calibration required.
--- Calibration chromatograms must be provided.
--- Retention Time (RT) Summary to include:
- RT measured for each target compound and surrogate at each standard concentration from three-point or five-point calibration
  OR RT measured for each target compound from three separate injections over a 72-hour period
- Mean RT for each target compound and surrogate (mean of three to five RTs from calibration
  OR mean of three RTs measured from injections over a 72-hour period)
- RT window for each target compound and surrogate

--- Calibration Factor (CF) Summary to include:
- CF calculated for each target compound and surrogate at each standard concentration
- Mean CF for each target compound and surrogate
- % Relative Standard Deviation (%RSD) of the CFs at each standard concentration for each compound

--- % Breakdown of endrin and % breakdown of DDT
--- Date and time of injection

*For multicomponent analytes, initial calibration is documented by:
--- Three-point or five-point calibration using mixture of Aroclors 1016 and 1260
--- A "one-point calibration" using a midrange standard must be run for all target multicomponent compounds
--- Calibration chromatograms must be provided.
--- Retention Time (RT) Summary:
- For Aroclors 1016 and 1260:
  -- RT measured for at least one major peak at each standard concentration from the three-point or five point calibration (same peak(s) at each concentration)
     OR RT measured for at least one major peak from three separate injections over a 72-hour period (same peak(s) used for each injection)
  -- Mean RT for the chosen major peak(s)
  -- RT window for the chosen major peak(s)

! Initial and Continuing Calibration Verification (ICV and CCV) documented by:
Note*: An instrument blank, a QC reference sample ("check sample"), and a midrange calibration standard is injected at the beginning and end of the run and at intervals in between (at least 1 per 20 samples or 1 per batch if batch is less than 20 samples. 1 per 10 samples is preferred.) For PCBs only Aroclors 1016 and 1260 need be injected unless there are specific known target PCBs*

at the site. If so, all targeted PCBs should be injected.

--- Chromatograms for midpoint standard and blank

--- Absolute RT for each single component analyte and major peak(s) of each multicomponent analyte in the midrange standard (and comparison to RT window established at calibration)

--- Percent Difference (%D) between calculated concentration and nominal ("true") concentration of each target analyte in the QC reference sample

--- %D between RF or CF of each single component analyte and major peak(s) of each multicomponent analyte in the midrange standard

- For multicomponent analytes run at midrange concentration only:
  - -- RT measured for three to five major peaks from "one-point calibration" run
    OR RT measured for at least one major peak from three separate injections over a 72-hour period (same peak(s) used for each injection)
  - -- Mean RT for the chosen major peak(s)
  - -- RT window for the chosen major peak(s)

--- Calibration Factor (CF) Summary to include:

- CF calculated for each target compound (total area of all peaks used for quantitation) at each standard concentration (or from each of three injections)
  OR CF calculated for three to five major peaks of each target compound from calibration run of midpoint standard
- Mean CF for each target compound (for analytes run at multiple concentrations or injected three times over a 72-hour period only)
- % Relative Standard Deviation (%RSD) of the CFs for each compound (for analytes run at multiple concentrations or injected three times over a 72-hour period only)

--- % Breakdown of endrin and % breakdown of DDT

--- Date and time of injection

! Method blank summary and chromatograms

! Detection/quantitation limit for each compound (in each sample)

! Surrogate recoveries for samples, blanks, and spikes

! Matrix spike/matrix spike duplicate (MS/MSD) analysis (minimum of 1 per 20 samples or 1 per batch of less than 20 samples for each matrix)
OR For medium to high concentration soil and waste samples, laboratory duplicates may be substituted for the MS/MSD.

! **Raw Data** for each sample, standard, field duplicate, blank, matrix spike, and matrix spike duplicate, including dilutions made, preparatory records, and chromatograms

! Confirmation of detection **required**: on second GC column *OR* by GC/MS

--- Chromatograms for samples, blanks, spikes, and standards for confirmation run on second column must be provided.

--- <u>If confirmation is done by Gas Chromatography/Mass Spectroscopy (GC/MS), the following information (relevant to GC/MS analysis) should also be provided:</u>

- Tuning criteria and results (instrument performance check)
- Calibration records (including total ion chromatogram)
- Chromatograms for samples and method blank
- QC reference sample for detected compounds
- Mass spectra for samples, QC reference sample, and blank, including reference spectra for

detected compounds

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APPENDIX III

Nature of the SW-846 Methods Manual

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Status and Summary of SW-846 Updates

Nature of the SW-846 Methods Manual

ABOUT SW-846[53]

The publication *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846),* contains in one reference the sampling and analytical methods approved by the U.S. Environmental Protection Agency (EPA) for sampling and analysis under Subtitle C [and Subtitles D and X] of the Resource Conservation and Recovery Act (RCRA). SW-846 provides state-of-the-art analytical test methods for a wide array of inorganic and organic constituents, as well as procedures for field and laboratory quality control, sampling, and [hazardous waste] characteristics testing (toxicity, ignitability, reactivity, and corrosivity). The methods are intended to promote accuracy, sensitivity, specificity, precision, and comparability of analyses and test results.

Several of the hazardous waste regulations under Subtitle C of RCRA require that specific methods described in SW-846 be employed for certain applications. In other situations, SW-846 functions as a guidance document setting forth acceptable, although not required, methods to be implemented by the user, as appropriate, to meet RCRA-related sampling and analysis needs. (Note: EPA plans, in the near future, to remove many required uses of SW-846 from the RCRA regulations.)

Organization and Format of SW-846

SW-846 is divided into two volumes and thirteen chapters. Volume I focuses on laboratory activities and is divided into three sections: IA, IB and IC. Volume IA provides an overview of quality control procedures (Chapter One), guidance on the selection of appropriate test methods (Chapter Two), and analytical methods for inorganic species, primarily metals (Chapter Three). Volume IB provides methods for organic analytes (Chapter Four). Volume IC includes a variety of test methods for miscellaneous analytes (Chapter Five), properties (Chapter Six), and procedures for evaluating a waste for a hazardous waste characteristic (Chapters Seven and Eight). Volume II provides guidance on sampling plan design and implementation (Chapter Nine), field sampling methods (Chapter Ten), ground water monitoring (Chapter Eleven), land treatment monitoring (Chapter Twelve), and incineration (Chapter Thirteen).

Chapter One[54] and the methods should be reviewed <u>together</u> to gain a thorough understanding of the necessary quality control and the means to implement it. Most of the analytical methods are separated into distinct modular procedures describing specific, independent analytical operations. These include extraction, digestion, cleanup, and determination. This format allows linking of the various steps in the analysis according to the type of sample (e.g., water, soil, sludge, still bottom); analyte(s) of interest, needed sensitivity, and available analytical instrumentation. However, Chapters Five (Miscellaneous) and Six (Properties) give complete methods which are not amenable to such segmentation to form discrete procedures. **The method selection chapter (Chapter Two) presents a comprehensive discussion of the application of SW-846 methods to various matrices during the determination of groups of analytes or specific analytes. It can be used by the chemist to construct the correct analytical method from an array of SW-846 procedures which cover the matrix, analyte, and concentration of interest.**

SW-846 Updates

[53]"About SW-846," SW-846 on CD-ROM, Version 2.0*: Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods*, SW-846, Third Edition**,** Final Update III, pp. 1-4. (Emphasis added.)

[54]SW-846 Chapter One is reprinted as Part IV of this IDEM Guidance Document: "Quality Assurance/Quality Control Principles and QAPP Preparation."

SW-846 is a "living document" that changes as new information and data are developed. Advances in analytical instrumentation and techniques are continually reviewed by [EPA] and periodically incorporated into SW-846 to support changes in the regulatory program and improve method performance. Thus, [EPA] periodically revises methods or incorporates new methods as updates to the SW-846 methods manual. . . .Such a revision to SW-846 is first released by [EPA] as a "proposed update," whereby a Federal Register Notice (FRN) is published proposing the addition of the methods as an update to SW-846. During the public comment period, the regulated community and any other interested members of the public are invited to submit comments on methods and chapters contained in the update. After [EPA] has addressed all comments, the final update is published and distributed, and an FRN is published to incorporate it as a final rule into the RCRA, Subtitle C regulations. (Note: This formal rulemaking process will not be necessary for all updates once EPA removes many of the required uses of SW-846 from the RCRA regulations, as planned for the near future.)

Several final SW-846 updates have been released by [EPA] since the Third Edition of SW-846 was originally published [in September 1986]. To date [EPA] has revised the Third Edition of SW-846 with Update I (pages dated September 1992), Update IIA (pages dated August 1993), Update II (pages dated September 1994), Update IIB (pages dated January 1995), and Update III (pages dated December 1996). . . . Final Update III was promulgated on June 13, 1997 (see 62 FR 32452), and included the addition of many new and revised methods. Update III also included the removal of sixteen methods from SW-846, including the removal of many packed-column methods.

SW-846 Method Numbers

SW-846 methods are identified by a four digit number, [e.g.], Method 9035 or Method 8280. When published as a new method, the number does not include a letter suffix. Each time a method is revised and promulgated as part of an update, it receives a new letter suffix. For example, a suffix of "A" indicates revision one of that method, a suffix of "B" indicates revision two, etc. (Note: the revision number [of the individual analytical method] does not necessarily reflect the update number [of SW-846]. **In order to properly document the SW-846 method used during analysis, the entire method number, including the suffix letter designation, must be identified by the analyst.** In addition, a method reference found within the RCRA regulations; the text of SW-846 methods and chapters; [and IDEM guidance documents, correspondence, and Broad Agency Announcements] always refers to the latest promulgated version of the method, even if the method number at those locations does not include the appropriate letter suffix.

A summary follows of the status of the final updates with regard to State of Indiana Hazardous Waste Management Rules, 329 IAC 3.1, and Indiana Used Oil Management Rules, 329 IAC 13, of the Indiana Administrative Code:

STATUS OF PROMULGATED UPDATES IN RELATION TO INDIANA RULES			
SW-846 Update Package	**Date Listed on Methods**	**Date Adopted in Indiana Rules***	**Revisions Included**
Final Update I	July 1992	August 17, 1996 (1995 Annual Update)	***Chapter Text Revisions:*** • Chapter One: "Quality Control" (Rev. 1) • Chapter Two: "Choosing the Correct Procedure" (Rev. 1) • Chapter Three: "Metallic Analytes" (Rev.1) • Chapter Four: "Organic Analytes" (Rev. 1) • Chapter Seven: "Introduction and Regulatory Definitions" for RCRA Characteristics (Rev. 1) ***Method Revisions:*** *METALS PREP* • 3005A, • 3010A, • 3020A, • 3050A *METALS* • 6010A, • 7000A, • 7061A, • 7196A, • 7760A *ORGANIC PREP* • 3500A, • 3510A, • 3520A, • 3540A, • 3580A, • 3600A, • 3610A, • 3611A, • 3620A, • 3630A, • 3650A, • 3660A, • 5030A *ORGANIC* • 8000A, • 8010A, • 8015A, • 8030A, • 8040A, • 8150A, • 8240A, • 8270A *GENERAL CHEMISTRY* • 9010A, • 9020A, • 9030A *PROPERTIES* • 1330A, • 9041A, • 9045A, • 9090A *CHARACTERISTICS* • 1020A, • 1310A, • HCN, • H_2S ***Methods Added*** *METALS* • 7081, • 7211, • 7381, • 7430, • 7461, • 7761, • 7780, • 7951 *ORGANIC* • 8011, • 8021, • 8070, • 8110, • 8141, • 8260 *MISC. METHODS* • 9013, • 9021, • 9031 *CHARACTERISTICS* • 1311

*****The "Annual Update" referred to in the Indiana Rules column refers to updates of 329 IAC 3.1, the Indiana state hazardous waste rules. It should not be confused with Final Updates of SW-846.

STATUS OF PROMULGATED UPDATES IN RELATION TO INDIANA RULES			
SW-846 Update Package	**Date Listed on Methods**	**Date Adopted in Indiana Rules***	**Revisions Included**
Final Update IIA	August 1993	August 17, 1996 (1995 Annual Update)	***Method Added*** *(This one method comprises IIA)* • 4010 Pentachlorophenol - Immunoassay Screen
***The "Annual Update" referred to in the Indiana Rules column refers to updates of 329 IAC 3.1, the Indiana state hazardous waste rules. It should not be confused with Final Updates of SW-846.			

STATUS OF PROMULGATED UPDATES IN RELATION TO INDIANA RULES			
SW-846 Update Package	**Date Listed on Methods**	**Date Adopted in Indiana Rules***	**Revisions Included**
Final Update II	September 1994	August 17, 1996 (1995 Annual Update)	***Chapter Text Revisions:*** • Chapter Two (Rev. 2) • Chapter Three (Rev.2) • Chapter Four (Rev. 2) • Chapter Five: "Miscellaneous Test Methods" (Rev. 1) • Chapter Six: "Properties" (Rev. 1) • Chapter Seven(Rev. 2) • Chapter Eight: "Methods for Determining Characteristics" (Rev. 1) ***Method Revisions:*** *METALS* • 7060A, • 7080A, • 7131A, • 7470A, • 7471A, • 7741A *ORGANIC PREP* • 3510B, • 3520B, • 3540B, • 3550A, • 3600B, • 3630B, • 3640A, • 5040A *ORGANIC* • 8010B, • 8020A, • 8021A, • 8080A, • 8120A, • 8141A, • 8150B, • 8240B, • 8250A, • 8260A, • 8270B *MISC. METHODS* • 9020B, • 9071A *PROPERTIES* • 9040A, • 9045B *CHARACTERISTICS* • HCN, • H_2S ***Methods Added*** *INORGANIC PREP & METALS* • 3015, • 3051, • 6020, • 7062, • 7742 *ORGANIC PREP & ORGANIC* • 3541, • 3665, • 8031, • 8032, • 8061, • 8081, • 8121, • 8151, • 8290, • 8315, • 8316, • 8318, • 8321, • 8330, • 8331, • 8410 *MISC. METHODS* • 5050, • 9056, • 9075, • 9076, • 9077, • 9253 *PROPERTIES* • 9096
***The "Annual Update" referred to in the Indiana Rules column refers to updates of 329 IAC 3.1, the Indiana state hazardous waste rules. It should not be confused with Final Updates of SW-846.			

STATUS OF PROMULGATED UPDATES IN RELATION TO INDIANA RULES			
SW-846 Update Package	**Date Listed on Methods**	**Date Adopted in Indiana Rules***	**Revisions Included**
Final Update IIB	January 1995	August 17, 1996 (1995 Annual Update)	***Chapter Text Revision:*** • Chapter Six: "Properties" (Rev. 2) ***Method Revisions:*** *PROPERTIES* • 9040B, • 9045C
***The "Annual Update" referred to in the Indiana Rules column refers to updates of 329 IAC 3.1, the Indiana state hazardous waste rules. It should not be confused with Final Updates of SW-846.			

STATUS OF PROMULGATED UPDATES IN RELATION TO INDIANA RULES			
SW-846 Update Package	**Date Listed on Methods**	**Date Adopted in Indiana Rules***	**Revisions Included**
Final Update III	December 1996	To be adopted in the 1998 Annual Update. Projected effective date: January 1999	***Chapter Text Revision:*** • Chapter Two (Rev. 3) • Chapter Three (Rev. 3) • Chapter Four (Rev. 3) • Chapter Five (Rev. 2) • Chapter Six (Rev. 3) • Chapter Seven (Rev. 3) • Chapter Eight (Rev. 2) • Chapter Ten: "Sampling Methods" (Rev. 1) ***Method Revisions:*** *INORGANIC PREP & METALS* • 3040A, • 3050B, • 3060A, • 6010B *ORGANIC PREP* • 3500B, • 3510C, • 3520C, • 3540C, • 3550B, • 3600C, • 3610B, • 3611B, • 3620B, • 3630C, • 3650B, • 3660B, • 3665A, • 5030B, • 5041A *ORGANIC* • 4010A, • 8000B, • 8015B, • 8021B, • 8032A, • 8061A, • 8070A, • 8081A, • 8151A, • 8260B, • 8270C, • 8275A, • 8280A, • 8315A, • 8321A *MISC. METHODS & PROPERTIES* • 9010B, • 9012A, • 9030B, • 9095A *CHARACTERISTICS* • HCN, • H_2S ***Methods Added*** *INORGANIC PREP & METALS* • 3031, • 3052, • 7063, • 7199, • 7472, • 7521, • 7580 *ORGANIC PREP* • 3535, • 3542, • 3545, • 3560, • 3561, • 3585, • 5000, • 5021, • 5031, • 5032, • 5035 *ORGANIC* • 8033, • 8041, • 8082, • 8091, • 8111, • 8131, • 8325, • 8332, • 8430, • 8440, • 8520 *IMMUNOASSAY* • 4000, • 4015, • 4020, • 4030, • 4035, • 4040, • 4041, • 4042, • 4050, • 4051, • 8515 *MISC. METHODS* • 9014, • 9023, • 9034, • 9057, • 9210, • 9211, • 9212, • 9213, • 9214, • 9215, • 9078, • 9079

*****The "Annual Update" referred to in the Indiana Rules column refers to updates of 329 IAC 3.1, the Indiana state hazardous waste rules. It should not be confused with Final Updates of SW-846.

STATUS OF PROMULGATED UPDATES IN RELATION TO INDIANA RULES			
SW-846 Update Package	**Date Listed on Methods**	**Date Adopted in Indiana Rules***	**Revisions Included**
Final Update III, *continued*	December 1996	To be adopted in the 1998 Annual Update. Projected effective date: January 1999	***Methods Added**, continued* *PROPERTIES* • 1030, • 1120 *AIR EMISSIONS SAMPLING & SCREENING* • 0011, • 0023A, • 0031, • 0040, • 0050, • 0051, • 0060, • 0061, • 0100 ***Methods DELETED from SW-846*** *ORGANIC PREP* • 5040/5040A *ORGANIC* • 8010/8010A/8010B, • 8020/8020A, • 8030/8030A, • 8040/8040A, • 8060, • 8080/8080A, • 8090, • 8110, • 8120/8120A, • 8140, • 8150/8150A/8150B • **8240/8240A/8240B**, • 8250/8250A *MISC. METHODS* • 9200, • 9252/9252A
*****The "Annual Update" referred to in the Indiana Rules column refers to updates of 329 IAC 3.1, the Indiana state hazardous waste rules. It should not be confused with Final Updates of SW-846.			

PROPOSED UPDATE NOTICE		
SW-846 Update Package	**Date Listed on Methods**	**Proposed Revisions**
Proposed Update IVA ***(Salmon-colored pages)***	January 1998	• Revised Chapter Two: "Choosing the Right Method" • Revised Chapter Three and new/revised methods for inorganic prep and analyses; • Revised Chapter Four and new/revised methods for organic analyses; • Revised Chapter Five and one new method for miscellaneous analyses (Turbidimetric Screening for Total Recoverable Petroleum Hydrocarbons in Soil) • **44 Methods Proposed for Removal from SW-846:** • 3810 Headspace (Now replaced by 5021); • All flame AA methods to be removed and integrated into revised Method 7000B; • All graphite furnace AA methods to be removed and integrated into new Method 7010.

Update IV will not be subject to the extensive comment period and promulgation process required for previous Editions and Updates of SW-846. Update IV is being created under the auspices of the Methods Reinvention Rule. Updates are now released as Notices of Data Availability (NODA) in the Federal Register and include methods that are being considered for addition to SW-846. They are subject to a 30-day public comment period.

Update IV will be released in two parts: Update IVA and Update IVB.

Update IVA was published as a NODA in the *Federal Register* on May 8, 1998 (63 *FR* 25430). The comment period closed on June 22, 1998. It contains inorganic methods that were completed from 1996-1998.

EPA's Office of Solid Waste (OSW) is currently working on a second part of Update IV, IVB, which includes primarily organic methods, to be published as another NODA. It is expected to appear in the Federal Register in the spring or early summer of 1999. The Update could possibly contain up to 50 methods, 20 new methods, 26 revised methods, and 4 air methods to be incorporated by reference.

When and how the Update IV methods will be incorporated into SW-846, will depend on the progress of the Methods Reinvention Rule. This rule is intended to remove the unnecessary requirements to use SW-846 methods in the RCRA regulations and to allow the OSW to issue Updates to SW-846 as **guidance** per the original intent of the document.*

*Reference: OSW Methods Team web page: http://www.epa.gov/epaoswer/hazwaste/test/rcra.pdf

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APPENDIX IV

PERFORMANCE BASED MEASUREMENT SYSTEMS

Performance Based Measurement Systems

Performance-Based Measurement Systems (PBMS) allow flexibility in the selection of analytical methods and control criteria **to meet the data quality objectives of the project or program.** PBMS is a system in which the data quality needs, regulatory mandates, or limitations of a program or project are specified and serve as the criteria for selecting analytical appropriate methods to meet those needs in a cost effective manner. This is in contrast to mandating particular analytical methods, a particular methods manual, or a particular statement of work with set control criteria to be followed in a "cookbook" fashion for compliance with regulatory requirements, whether or not scientifically valid or practical for the specific site or project.

The Performance Based Measurement System concept was developed by a workgroup of the Environmental Monitoring Management Council within EPA. In the October 6, 1997, Federal Register, EPA published an intent to implement a PBMS system for environmental monitoring in all media programs to the extent feasible. (See *62 FR 52098*.) Unnecessary methods mandates are to be removed, opening the door to a much larger universe of analytical method possibilities. Nevertheless, it remains necessary for environmental professionals, including regulators, to have some means by which to judge a method's scientific rigor, as well as its efficacy in providing environmental data for a specific environmental project. If certain basic elements are included in the written documentation, it is possible to assess a method's validity and effectiveness.

The following, from an article by Barry Lesnik and Paul Marsden of EPA's Office of Solid Waste, neatly describes the objectives of analytical method development as "simple adaptations of the scientific method" that can be summed up in three steps. These steps can be used to evaluate the validity of a method under PBMS as well as to evaluate newly developed methods:

Step 1. Identify the scope and application of the method: what is this method supposed to accomplish?

Step 2. Develop a procedure that will generate data that are consistent with the intended scope and application of the methods.

Step 3. Establish appropriate quality control procedures that will ensure that when the proposed procedure is followed, the method will generate the appropriate data from Step 2 that will meet the criteria established in Step 1.[55]

If the method documentation demonstrates that the above three steps have been accomplished, the method will be evaluated as satisfactory. It is recommended that the elements listed in the following table are included in the written method to provide the demonstration.[56] Elements that are bolded are considered key; their inclusion is highly recommended:

[55]Barry Lesnik and Paul Marsden, "Demystifying Methods Development," *Environmental Lab*, July 1995, p. 16.

[56]Adapted from: (1) Lesnik and Marsden, Ibid., p. 18.; and (2) the Environmental Monitoring Management Council format for analytical methods as stated in EPA document PBMA-S0001, "EPA Performance Based Measurement System Draft Generic Checklists."

Recommended Elements to be Included in Analytical Methods Submitted to IDEM for PBMS Approval	
1	**Scope and Application of Method**
2	**Summary of Method**
3	**Analytical Approach**
4	**Method/Instrument Sensitivity**
5	Method Optimization and Ruggedness Testing Matrix Suitability
6	**Matrix Suitability**
7	**Detection and Quantitation Limits (and upper performance range) in Various Matrices**
8	**Effect of Interferences (and type of interferences observed or expected)**
9	Definitions
10	Safety Precautions for Analysts
11	**Sample Collection, Preservation, and Storage**
12	**Quality Assurance/Quality Control Procedures and Requirements**
13	**Instrumentation, Equipment,** and Supplies
14	**Reagents and Standards**
15	**Sample Preparation Procedures (including digestion, extraction, etc.)**
16	**Calibration and Standardization**
17	**Analytical Procedures**
18	**Data Analysis and Calculations**
19	**Accuracy, Precision, and Repeatability in a Clean Matrix (e.g., reagent water)**
20	Lab Reproducibility (Multiple Operators and Multiple Labs)
21	**References**
22	Tables, Diagrams, and Flowcharts as appropriate
23	Pollution Prevention
24	Waste Management and Disposal
Additional Information to Include When Data Generated by Method is Submitted (Project Specific Information)	
25	**Applicability of Method to Current Environmental Project/Project Objective**
26	**Method Optimization or Modification to Address Project DQOs or Site Matrices**

EPA is in the process of developing draft "Performance Based Measurement System Generic Checklists" to aid in evaluating analytical method validity and performance. The intention is that the checklists will be applicable to all environmental programs/media and to any type of method (screening, preparation, determinative analysis). The focus of the checklists, as they will be applied in Indiana, is to help determine if a "non-standard" method or modification of a standard method is appropriate for meeting the data quality objectives of a particular environmental project.

The EPA checklists are not yet available to the public. IDEM has prepared preliminary worksheets for PBMS evaluation by adapting early drafts of the EPA checklists. The Indiana Performance Based Measurement System Generic Worksheets are provided on the following pages. They (or their equivalent) should be used to evaluate new or modified methods used to generate data submitted to IDEM.

Indiana PBMS Worksheet for Initial Demonstration of Method Performance*

**Note: Provide a separate worksheet for each matrix evaluated. For multi-analyte methods with criteria or response varying by analyte, provide a separate worksheet for each analyte.*

Date:

Laboratory Name & Address:

Facility Name:

Project Type *(e.g., Risk Assessment, Closure, etc.)***:**

IDEM Program *(e.g., VRP, Hazardous Waste, UST, Solid Waste, etc.)***:**

Brief Description of Project Objective and DQO:

Analyte, Class of Analytes, or Other Measured Parameters *(e.g., barium, trace metals, benzene, volatile organics, dermal corrosion, etc.* **Include CAS Number(s), where available):**

Matrix or Medium *(e.g., soil, sediment, sludge, waste solid, leachate, ground water,, other)*:

Title of PBMS Method *(attach copy of written method)***:**

Title of Reference Method (or Method Modified), if applicable *(include method no., revision no., date; attach copy)***:**

Attach additional sheets as necessary.

Initial Demonstration of Method Performance						
Method Element or Criterion Category		**Performance Criteria Based on:**				**Results Obtained** *(e.g., 95% RPD, Satisfactory, Yes, Not provided etc.)*
		Reference Method		**Data/Measurement Quality Objective**		
		(✓)	***Name or No.***	***(✓)***	***Description***	
1.	Scope and Application of Method					
2.	Summary of Method *(include summary of modifications if based on reference method)*					
3.	Analytical Approach					
4.	Method/Instrument Sensitivity					
5.	Method Optimization/ Ruggedness					
6.	Matrix Suitability					

Initial Demonstration of Method Performance						
Method Element or Criterion Category		**Performance Criteria Based on:**				**Results Obtained** *(e.g., 95% RPD, Satisfactory, Yes, Not provided etc.)*
		Reference Method		**Data/Measurement Quality Objective**		
		(✓)	***Name or No.***	***(✓)***	***Description***	
7.	Detection and Quantitation Limits					
8.	Performance Range					
9.	Types of Interferences					
10.	Effects of Interferences					
11.	Definitions					
12.	Sample Collection					
13.	Sample Preservation					
14.	Sample Storage					
15.	Quality Assurance/Quality Control					
	A. Criterion 1_____					
	B. Criterion 2_____					
	C. Criterion 3_____					
	D. Criterion 4_____					
	E. Criterion 5_____					
	F. Criterion 6_____					
	G. Criterion 7_____					
	H. Criterion 8_____					
	I. Criterion 9_____					
	J. Criterion 10_____					
16.	Instrumentation					
17.	Equipment					
18.	Supplies					
19.	Reagents					
20.	Standards					

Initial Demonstration of Method Performance						
Method Element or Criterion Category		**Performance Criteria Based on:**				**Results Obtained** *(e.g., 95% RPD, Satisfactory, Yes, Not provided etc.)*
		Reference Method		**Data/Measurement Quality Objective**		
		(✓)	***Name or No.***	***(✓)***	***Description***	
21.	Calibration					
22.	Calibration Verification					
23.	Sample Preparation					
24.	Sample Cleanup (if applicable)					
25.	Analytical Procedures					
26.	Qualitative Procedures					
27.	Calculations and Quantitation					
28.	Accuracy or Bias Determination					
29.	Precision Determination					
30.	Repeatability Determination					
31.	Reproducibility between labs					
32.	References					
34.	Analyst Safety Considerations					
35.	Pollution Prevention					
36.	Waste Management & disposal					
37.	Reviewer's Summary: *(Is method appropriate for project DQOs? Etc.)*					

Name **Signature** **Date**

Name	Signature	Date
Name	**Signature**	**Date**

PBMS Worksheet for Continuing Demonstration of Method Performance

Date:

Laboratory Name & Address:

Facility Name:

Project Type *(e.g., Risk Assessment, Closure, etc.)**:***

IDEM Program *(e.g., VRP, Hazardous Waste, UST, Solid Waste, etc.)***:**

Brief Description of Project Objective and DQO:

Analyte, Class of Analytes, or Other Measured Parameters *(e.g., barium, trace metals, benzene, volatile organics, dermal corrosion, etc.* **Include CAS Number(s), where available):**

Matrix or Medium *(e.g., soil, sediment, sludge, waste solid, leachate, ground water,, other)*:

Title of PBMS Method and Date of Initial Demonstration

Title of Reference Method:

Attach additional sheets as necessary.

Continuing Demonstration of Method Performance						
Method Element or Criterion Category		**Performance Criteria Based on:**				**Results Obtained** *(e.g., 95% RPD, Satisfactory, Yes, Not provided etc.)*
		Reference Method		**Data/Measurement Quality Objective**		
		(✓)	***Name or No.***	***(✓)***	***Description***	
1.	Summary of Method *(include summary of modifications if based on reference method or if modified since Initial Demonstration.* ***Note: Major modification requires <u>new</u> Initial Demonstration)***					
2.	Matrix Suitability					
3.	Detection and Quantitation Limits					

Continuing Demonstration of Method Performance						
Method Element or Criterion Category		**Performance Criteria Based on:**				**Results Obtained** *(e.g., 95% RPD, Satisfactory, Yes, Not provided etc.)*
		Reference Method		**Data/Measurement Quality Objective**		
		(✓)	***Name or No.***	***(✓)***	***Description***	
4.	Performance Range					
10.	Types of Interferences					
10.	Effects of Interferences					
11.	Quality Assurance/Quality Control					
	A. Criterion 1_____					
	B. Criterion 2_____					
	C. Criterion 3_____					
	D. Criterion 4_____					
	E. Criterion 5_____					
	F. Criterion 6_____					
	G. Criterion 7_____					
	H. Criterion 8_____					
	I. Criterion 9_____					
	J. Criterion 10_____					
12.	Standards (concentrations & source)					
13.	Calibration					
14.	Calibration Verification					
22.	Sample Preparation					
23.	Sample Cleanup (if applicable)					
24.	Analytical Procedures					
25.	Qualitative Procedures					
26.	Calculations and Quantitation					
27.	Performance Evaluation (PE) Studies Results (if applicable)					
	A. Study Sponsor and Title					

Continuing Demonstration of Method Performance						
Method Element or Criterion Category		**Performance Criteria Based on:**				**Results Obtained** *(e.g., 95% RPD, Satisfactory, Yes, Not provided etc.)*
		Reference Method		**Data/Measurement Quality Objective**		
		(✓)	***Name or No.***	***(✓)***	***Description***	
	B. Study Number					
28.	Reproducibility between labs (if applicable)					
	A. Round Robin Sponsor and Title					
	B. Round Robin Number					
35.	Reviewer's Summary: *(Does method continue to be appropriate for project DQOs and matrices? New observations or developments?Etc.)*					

Name	**Signature**	**Date**
Name	**Signature**	**Date**
Name	**Signature**	**Date**

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APPENDIX V

DEFINITIONS and ACRONYMS
Used in this Document

Definitions and Acronyms Used in this Document

AA: **Atomic Absorption [spectroscopy]**.

Accuracy: **The closeness of agreement between an observed value and an accepted reference value.** When applied to a set of observed values, accuracy will be a combination of a random error component and of a systematic error (or bias) component.

Analytical Shift: **See Twelve-hour analytical shift.**

ANSI: **American National Standards Institute.**

ASQ: **American Society for Quality.** Organization formerly known as the ASQC.

ASQC: **American Society for Quality Control.** Former name of the ASQ.

Batch: **A group of samples** which behave similarly with respect to the sampling or the testing procedures being employed and **which are processed as a unit**. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch. This is also known as a **case** of samples.

BFB: **4-Bromofluorobenzene.** The compound used to establish mass spectral instrument performance for analysis of volatile organic compounds.

Bias: **The deviation due to matrix effects of the measured value (x_s - x_u) from a known spiked amount**. Bias can be assessed by comparing a measured value to an accepted reference value in a sample of known concentration or by determining the recovery of a known amount of contaminant spiked into a sample (matrix spike). Thus, the bias (B) due to matrix effects based on a matrix spike is calculated as:

$$B = (x_s - x_u) - K$$

where:

x_s = measured value for spiked sample,
x_u = measured value for un-spiked sample, and
K = known value of the spike in the sample.

Blank: See Equipment Rinsate, Field Blank, Instrument Blank, Method Blank, Trip Blank..

BOD: **Biochemical Oxygen Demand**. A measure of the amount of oxygen consumed in the biological processes that break down organic matter in water. Used to estimate the degree of contamination in water supplies from sewage and industrial wastes.

Breakdown: **A measure of the decomposition of certain analytes into by-products during analysis.** For the purposes of this document, it specifically refers to degradation of DDT and Endrin during analysis of pesticides by gas chromatography.

BTU: **British Thermal Unit** (reported as BTU/lb). A measure of the heating value of fuels.

Calibration Blank: A volume of acidified reagent water (for metals analysis) or pure solvent (for some organics analyses) which is taken through the analytical process exactly like the standards and samples, but not taken through the sample preparation process. The calibration blank is run directly after initial calibration and after each continuing calibration standard.

Calibration standards: A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve).

CCC: **Calibration Check Compound**. Used to verify calibration in analysis of volatile and semivolatile organic compounds by SW-846 gas chromatography/mass spectrometry methods. **The purpose of the CCCs is to evaluate the calibration from the standpoint of the integrity of the system**. High variability for these compounds may be indicative of system leaks or reactive sites on the column.

CCV: **Continuing Calibration Verification [Standard]**. Used to assure calibration accuracy during each analysis run. It must be run for each analyte as described in the particular analytical method. At a minimum, it should be analyzed at the beginning of the run and after the last analytical sample. Its concentration should be at or near the mid-range levels of the calibration curve.

CERCLA: **Comprehensive Environmental Response, Compensation, and Liability Act.** Often referred to as **Superfund.**

Check Standard: A solution containing a known concentration of analyte derived from externally prepared test materials. The check standard is obtained from a source external to the laboratory and is used to check laboratory performance.

CLP: U.S. EPA **Contract Laboratory Program**. Analytical protocol commonly used for CERCLA sites.

COD: **Chemical Oxygen Demand.** A measure of the oxygen required to oxidize all compounds, both organic and inorganic, in water.

Control Sample: A **QC sample** introduced into a process to monitor the performance of the system..

D001: RCRA hazardous waste code for the Characteristic of **Ignitability**, as defined in 40 CFR 261.21 and in SW-846 Chapter Seven.

D002: RCRA hazardous waste code for the Characteristic of **Corrosivity**, as defined in 40 CFR 261.22 and in SW-846 Chapter Seven.

D003: RCRA hazardous waste code for the Characteristic of **Reactivity**, as defined in 40 CFR 261.23 and in SW-846 Chapter Seven.

D004 - D043: RCRA hazardous waste codes for the Characteristic of **Toxicity** (specific organic and inorganic analytes), as defined in 40 CFR 261.24 and as determined by the **Toxicity Characteristic Leaching Procedure (TCLP),** SW-846 Method 1311.

Data Validation: The **process of evaluating environmental data against the project DQOs** to make sure that the objectives are met and whether the results make sense in the context of the study objectives. The data reviewed will include field records, field QC data, analytical results, and lab QC data.

Decision Error: An error made when drawing an inference from an environmental data set, such that variability or bias in the data misleads the decision maker into **drawing a false conclusion about the actual condition of the site being assessed**.

DFTPP: **Decafluorotriphenylphosphine.** The compound used to establish mass spectral instrument performance for analysis of semivolatile organic compounds.

Dissolved metals: The concentration of metals determined in a sample after the sample is filtered through a 0.45-µm filter.

DQOs: **Data Quality Objectives**. Qualitative and quantitative statements derived from the outputs of each step of the **DQO Process** that:

1) Clarify the project objective;
2) Define the most appropriate type of data to collect;
3) Determine the most appropriate conditions from which to collect the data; and
4) Specify acceptable levels of decision errors that will be used as the basis for establishing the quantity and quality of data needed to support the decision.

The DQOs are used to develop a scientific and resource-effective sampling design.

DQO Process: A **series of planning steps based on the Scientific Method** that is designed to ensure that the type, quantity, and quality of environmental data used in decision making are appropriate for the intended application. The steps of the DQO Process are illustrated in Figure 2 (Section II).

Duplicate: See Matrix Duplicate, Field Duplicate, Laboratory Duplicate, Matrix Spike Duplicate.

ECD: **Electron Capture Detector**. Used for some gas chromatographic analyses.

EMMC: **Environmental Monitoring Management Council.** An EPA workgroup.

EQL: **Estimated Quantitation Limit.** The **lowest concentration that can be reliably achieved** within specified limits of precision and accuracy **during routine laboratory operating conditions**. Use of the word "estimated" emphasizes sample matrix dependence. (EQLs have replaced "PQLs"(Practical Quantitation Limits) in SW-846 methods.)

Equipment Blank: See Equipment Rinsate.

Equipment Rinsate: A **sample of analyte-free water which has been used to rinse the sampling equipment**. It is collected after completion of decontamination and prior to sampling. This blank is useful in documenting adequate decontamination of sampling equipment. Also known as the **equipment blank** or the **rinsate blank.**

External Standard Calibration: **The comparison of instrument responses from the sample to the responses from the target compounds in the calibration standards**. Sample peak areas (or peak heights) are compared to peak areas (or heights) of the standards. The ratio of the detector response to the amount (mass) of analyte in the calibration standard is defined as the calibration factor (CF).

Field Blank: Any sample submitted from the field and identified as a blank. **Trip blanks** and **equipment rinsates** are examples of field blanks**.**

Field Duplicates: Two **separate samples taken from the same source**, collected as close as possible to the same point in space and time, and used to document the precision of the sampling process. They are stored in separate containers, and analyzed independently.

GC: **Gas Chromatography**. Separation technique use for organic compounds that can be volatilized without being decomposed or chemically rearranged. (More properly called "gas-liquid chromatography.")

GC/ECD: **Gas Chromatography/Electron Capture Detector**.

GC/MS: **Gas Chromatography/Mass Spectrometry**.

GFAA: **Graphite Furnace Atomic Absorption** [spectroscopy].

Holding Time: The storage time allowed between sample collection and sample analysis (or between sample collection and extraction, and between extraction and extract analysis) when the designated preservation and storage techniques are employed.. Also referred to as **Sample Holding Time.**

HPLC: **High Performance Liquid Chromatography**. Separation technique useful for semivolatile and nonvolatile organic compounds.

ICP: **Inductively Coupled Plasma Atomic Emission Spectroscopy.** (Also "ICAP")

ICP/MS: **Inductively Coupled Plasma [Atomic Emission] Spectroscopy/Mass Spectrometry.**

IDL: **Instrumental Detection Limit.** The concentration equivalent to a signal due to the analyte which is equal to three times the standard deviation of a series of 7 replicate measurements of a reagent blank's signal at the same wavelength.

ICS: **Interference check sample**. A solution containing both interfering and analyte elements of known concentration that can be used to verify background and inter-element correction factors.

ICV: **Initial Calibration Verification [Standard]**: A certified or independently prepared solution used to verify the accuracy of the initial calibration. For ICP analysis, it must be run at each wavelength used in the analysis.

Internal Standard Calibration: **The comparison of instrument responses from the target compounds in the sample to the responses of specific standards added to the sample or sample extract prior to injection**. The ratio of the peak area (or height) of the target compound in the sample or sample extract to the peak area (or height) of the internal standard in the sample or sample extract is compared to a similar ratio derived for each calibration standard. The ratio is termed the **response factor (RF)**, or as the **relative response factor (RRF)** in certain methods

Laboratory Duplicate: An **intralaboratory split sample** used to document the precision of a method in a given sample matrix. Also called a **matrix duplicate.**

LCS: **Laboratory Control Sample.** A **known matrix spiked with compound(s) representative of the target analytes** used to document laboratory performance.

Linear Dynamic Range: The concentration range over which the analytical curve remains linear.

LPO: **Laboratory Project Officer**. The contact person at the laboratory who arranges analytical services and answers questions for the client submitting samples. Also called a Laboratory Project Manager.

Matrix: The component or **substrate** (e.g., surface water, ground water, soil, sediment, sludge, air) **which contains the analyte of interest**.

Matrix Duplicate: An **intralaboratory split sample** used to document the precision of a method in a given sample matrix. Also called a **laboratory duplicate.**

Matrix Spike: An **aliquot of sample spiked with a known concentration of target analyte(s)** used to document the bias of a method in a given sample matrix. The spiking occurs prior to sample preparation and analysis.

Matrix Spike Duplicates: **Intra-laboratory split samples spiked with identical concentrations of target analyte(s)** used to document the precision and bias of a method in a given matrix.. The spiking occurs prior to sample preparation and analysis. sample.

MDL: **Method Detection Limit.** A statistical construct intended to approximate the **minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero**. It is determined from analysis of a sample in a given matrix type containing the analyte.

Method Blank: An **analyte-free matrix to which all reagents are added in the same volumes or proportions as used in processing samples**. The method blank must be carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process. Also referred to as **preparation blank** or **reagent blank**.

For a method blank to be acceptable for use in a batch of samples, the concentration in the blank of any analyte of concern must be no higher than the highest of either:
(1) The detection limit, or
(2) Five percent of the regulatory limit for that analyte, or
(3) Five percent of the measured concentration in the sample.

MS: **Matrix Spike**.

MSA: **Method of Standard Additions**. The addition of known amounts of standard to one or more aliquots of the processed sample solution immediately prior to analysis. It is typically used to evaluate interferences. It compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The simplest version of this technique is the single-addition method. Improved results can be obtained by employing a series of standard additions. Also known as **Standard Addition**. For detailed instructions refer to SW-846 Method 7000A.

MSD: **Matrix Spike Duplicate.**

MS/MSD: **Matrix Spike/Matrix Spike Duplicate**. Synonymous with matrix spike duplicates.

Optimum concentration range A range, defined by limits expressed in concentration, below which scale expansion must be used and above which curve correction should be considered. This range will vary with the sensitivity of the instrument and the operating conditions employed.

Organic-Free Reagent Water: **Water in which an interferent is not observed at the method detection limit of the compounds of interest.** Organic-free reagent water can be generated by passing tap water through a carbon filter bed containing about 1 pound of activated carbon. A water purification system may be used to generate organic-free deionized water.

Alternatively, for volatiles use only: Organic-free reagent water may also be prepared by boiling water for 15 minutes and subsequently, while maintaining the temperature at 90°C, bubbling a contaminant-free inert gas through the water for 1 hour.

OAM: **Office of Air Management.**

OER: **Office of Environmental Response**.

OSHWM: **Office of Solid and Hazardous Waste Management.**

OWM: **Office of Water Management.**

PBMS: **Performance Based Measurement System**. **Flexibility in the selection of analytical methods and control criteria to meet the data quality objectives of the project or program.** (See full definition below.)

PCB: **Polychlorinated Biphenyls**.

Performance Based Measurement System **Flexibility in the selection of analytical methods and control criteria to meet the data quality objectives of the project or program.** A system in which the data quality needs, regulatory mandates, or limitations of a program or project are specified and serve as the criteria for selecting appropriate methods to meet those needs in a cost effective manner. (This is in contrast to mandating particular analytical methods with set control criteria to comply with regulatory requirements, whether or not scientifically valid or practical for the specific site or project.)

The Performance Based Measurement System concept was developed by a workgroup of the Environmental Monitoring Management Council withing EPA. In October 6, 1997, Federal Register, EPA published an intent to implement a PBMS system for environmental monitoring in all media programs to the extent feasible (62 FR 52098).

PQL: **Practical Quantitation Limit**. See EQL, Estimated Quanitation Limit.

Precision: **The agreement among a set of replicate measurements without assumption of knowledge of the true value**. Precision is estimated by means of duplicate/replicate analyses containing concentrations of analyte above the MDL, and may involve the use of matrix spikes. The most commonly used estimates of precision are the **relative standard deviation (RSD)**, used when three or more replicates are analyzed, and the **relative percent difference (RPD)**, used when only two samples are available.

The relative standard deviation, also called the coefficient of variation (CV), is calculated as:

$$\mathbf{RSD = CV = 100\ s\ \ x}$$

where **x** = the arithmetic mean, and **s** = standard deviation ,of the replicate measurements. The relative percent difference is calculated as:

$$\mathbf{RPD = 100\ [(x_1 - x_2)/\{(x_1 + x_2)/2\}]}$$

where $\mathbf{x_1}$ and $\mathbf{x_2}$ are the measured concentrations of the duplicate samples.

Preparation Blank: See Method Blank.

Project: **Single or multiple data collection activities that are related through the same planning sequence**. An organized set of activities within a program.

QA **Quality Assurance**. An integrated system of management activities involving planning, implementation, assessment, reporting, and quality improvement to ensure

that a process or service is of the type and quality needed and expected. For the purposes of this document, "process or service" refers to environmental projects and may include sampling design, sample collection, analysis, calculation, data validation, data verification, and data quality assessment.

QAO: **Quality Assurance Officer**. The person responsible for all QA/QC activities of a program or laboratory.

QA/QC **Quality Assurance/Quality Control**. See QA and QC.

QAPP **Quality Assurance Project Plan**. A formal document describing in comprehensive detail the necessary QA, QC, and other technical activities that must be implemented to ensure that the results of the work performed will satisfy the stated performance criteria. An orderly assemblage of detailed procedures designed to produce data of sufficient quality to meet the data quality objectives for a specific data collection activity. Sometimes referred to as **QAPjP**.

QC **Quality Control**. The overall system of technical activities that measures the attributes and performance of a process against defined standards to verify that they meet the stated requirements. Techniques and activities that are used to fulfill the requirements for quality. For the purposes of this document, QC will generally refer to measures taken in the field or in the laboratory to ensure or measure data quality.

QMP: **Quality Management Plan**. A formal document describing the management policies, objectives, principles, organizational authority, responsibilities, accountability, and implementation protocols of an agency, organization, program, or laboratory for ensuring quality in its products and utility to its users.

RCRA: The **Resource Conservation and Recovery Act**. Regulations governing solid and hazardous waste activities. RCRA **Subtitle C** refers to hazardous waste activities. RCRA **Subtitle D** refers to solid waste activities. RCRA **Subtitle I** refers to activities related to underground storage tanks.

Reagent Blank: See Method Blank.

Reagent Grade: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

Reagent Water: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water.

Reference Materials: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

RF: **Response Factor**. **A measure of the relative instrument response of a target analyte as compared to the instrument response of its internal standard**: The ratio of the peak area (or height) of the target compound in the sample or sample

extract to the peak area (or height) of the internal standard in the sample or sample extract. Sometimes referred to as **relative response factor**.

RRF: **Relative Response Factor**. See **Response Factor**.

RSD: **Relative Standard Deviation**. See **Precision.**

SAS: **Special Analytical Services**. Non-routine analyses.

SC: **Specific Conductance**. The potential for electrical conductivity of a water sample at 25°C expressed in mhos per centimeter ($ohm^{-1}cm^{-1}$). A indicator of ground water contamination by inorganic pollutants.

Sensitivity: (a) Atomic Absorption: The concentration in milligrams of metal per liter that produces an absorption of 1%; (b) Inductively Coupled Plasma (ICP): The slope of the analytical curve, i.e., the functional relationship between emission intensity and concentration.

SIM: **Selective Ion Monitoring.** In mass spectrometry, the monitoring of specific ions instead of full electron ionization (EI) spectra. Sensitivity is increased at the possible expense of qualitative accuracy.

% Solids: **Total percent solids, to be determined as specified in the analytical method being followed**. % Solids determinations are required in certain methods as a preliminary determination or to calculate dry-weight concentrations of analytes. Various techniques are specified depending on the analysis. Examples include oven drying of filtered solids at a specified temperature, application of pressure while filtering, and measurement of water evolved during extraction.

SPCC: **System Performance Check Compound**. Compounds checked for a minimum average response factor during initial calibration and calibration verification of GC/MS analyses. These compounds are chosen because they are typically the first compounds to demonstrate poor performance when problems arise in the analytical system. Possible problems include standard mixture degradation; contamination of injection port inlet, lines, or at the front end of the analytical column; active sites in the column or chromatographic system; non-optimal tuning, target compound degradation, and (in volatile analysis) non-optimal purge rate. The minimum RF check must be met before sample analysis begins.

Split Samples: Aliquots of sample taken from the same container and analyzed independently. In cases where aliquots of samples are impossible to obtain, field duplicate samples must be taken for the matrix duplicate analysis. These are usually taken after mixing or compositing and are used to document intra or inter-laboratory precision.

Standard Addition: The practice of adding a known amount of an analyte to a sample immediately prior to analysis. It is typically used to evaluate interferences. Also see MSA.

Standard Curve: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the analytical method or in the appropriate section of this manual. The calibration standards must be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic analyses.

Surrogate: An organic compound which is similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples. (Referred to as **system monitoring compounds** for analysis of volatiles in the CLP Statement of Work for Organics Analysis.)

Suspended metals: The concentration of metals determined in the **portion of a sample that is retained by a 0.45-µm filter.**

SVOA: **Semivolatile Organic Analysis**. Analysis of compounds amenable to analysis after extraction with solvent, usually implying analysis by GC/MS.

SVOC: **Semivolatile Organic Compound.** Compounds amenable to analysis after extraction with solvent. Used synonymously with **Base/Neutral/Acid (BNA) extractable compounds**. Analysis of extracts is usually performed by GC, GC/MS, or HPLC.

SW-846 **Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods,** U.S. EPA Publication **SW-846,** Third Edition, November 1986, and promulgated Updates. As of this writing, the current promulgated update is **Final Update III, December, 1996.** SW-846 is the standard methods manual commonly used by RCRA Subtitle C and D facilities, UST/LUST sites, and state and voluntary cleanup sites. This guidance manual is updated as new methods are developed based on advances in analytical techniques and technology.

TCLP: **Toxicity Characteristic Leaching Procedure**, **SW-846 Method 1311**. Analytical method mandated at 40 CFR 261.24 for determining if solid wastes exhibit the RCRA Characteristic of Toxicity (is classified as one of the RCRA hazardous waste codes D004 - D043).

Total metals: The **concentration of metals in an unfiltered sample** following acid or microwave-assisted acid digestion.

Trip Blank: A sample of analyte-free media taken from the laboratory to the sampling site and returned to the laboratory unopened. A trip blank is used to document contamination attributable to shipping and field handling procedures. This type of blank is useful in documenting contamination of volatile organics samples.

TKN: **Total Kjeldahl Nitrogen. Analysis for nitrogen compounds yielding the sum of free-ammonia and of organic nitrogen compounds of biological origin**, which are converted to (NH) SO under the analytical conditions.

TOX: **Total Organic Halides**. **Analysis that measures total concentration of the halogens chlorine, bromine, and iodine from organic compounds in the sample**. Fluorine cannot be determined by these methods. Specific compounds are not identified. However, certain techniques allow quantitation of individual halogens. (**X-** is commonly used to represent an unspecified halogen atom in formulas for organic compounds–hence the acronym **TOX**.)

TOC: **Total Organic Carbon**. **Analysis that measures total concentration of carbon from organic compounds in the sample**. Specific compounds are not identified. Carbonate and bicarbonate (inorganic carbon) are excluded.

Target Analyte: **Element or compound of interest for a specific environmental project.** Element or compound expected to be present in a waste stream or product, or known or suspected to be present in environmental media resulting from a spill or release of a waste stream or product. Also referred to as a **target compound**, or when sampling environmental media for contamination, as a **contaminant of concern (COC)**.

Alternatively, the target analytes for a site might comprise a standard list of compounds based on regulatory requirement or policy. Examples include Appendix IX of 40 CFR 264, the RCRA Subtitle C Groundwater Monitoring List, or Appendix II of 40 CFR 268, the RCRA Subtitle D List of Hazardous Inorganic and Organic Constituents. For a specific project, this is sometimes called a **target parameter list**.

Trace ICP: **Inductively Coupled Plasma Atomic Emission Spectroscopy analytical system in which instrumentation is modified or specialized to substantially lower detection limits.** Examples include axial orientation of the plasma torch or ICP/MS. These methods allow ICP analysis to be used in place of GFAA for elements or matrices in which standard ICP is not sufficiently sensitive.

Twelve-Hour Analytical Shift: **Samples (including QC samples) that can be analyzed in a 12-hour period.** The 12-hour analytical shift begins with the introduction of the calibration verification standard (or the MS tuning standard in MS methods). The shift ends after the completion of the analysis of the last sample or standard that can be injected (or purged, aspirated, etc.) within 12 hours of the beginning of the shift.

U.S. EPA **United States Environmental Protection Agency**. Also abbreviated as **USEPA**.

VOA: **Volatile Organics Analysis**. Analysis of compounds amenable to purge and trap technique (generally organic compounds boiling below 200°C), usually implying analysis by GC/MS.

VOC: **Volatile Organic Compound**. Compound amenable to purge and trap technique. Includes most organic compounds boiling below 200°C. Used synonymously with **purgeable compounds.**

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***This document draws heavily from the U.S. EPA document:

Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods, SW-846, Third Edition, Final Update III (SW-846, December 1996).

It also draws from EPA methodology and guidance in:

Methods for the Determination of Organic Compounds in Drinking Water, Supplement III (EPA/600/R-95/131, August 1995), and

USEPA Contract Laboratory Program Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration, OLM03.0, Revision OLM03.1 (August 1994).

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